

UC-NRLF



B 4 059 079

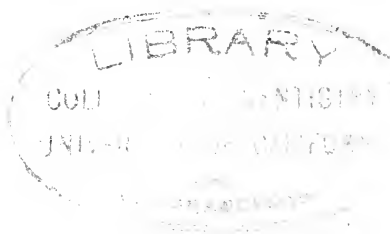
# INTRODUCTION TO PRACTICAL CHEMISTRY

A. M. KELLAS

OXFORD  
UNIVERSITY PRESS

Private Library  
Guy S. Millberry  
1043 Clayton St  
San Francisco

#6.





Digitized by the Internet Archive  
in 2007 with funding from  
Microsoft Corporation



OXFORD MEDICAL PUBLICATIONS

INTRODUCTION TO  
PRACTICAL CHEMISTRY

OXFORD : HORACE HART  
PRINTER TO THE UNIVERSITY

2842  
OXFORD MEDICAL PUBLICATIONS

# INTRODUCTION TO PRACTICAL CHEMISTRY

FOR MEDICAL, DENTAL, AND  
GENERAL STUDENTS

SPECIALLY ADAPTED TO MEET THE REQUIREMENTS OF THE  
CONJOINT BOARDS' EXAMINATION OF THE ROYAL COLLEGES  
OF PHYSICIANS AND SURGEONS, BUT SUITABLE FOR GENERAL  
USE IN SCHOOLS AND FOR PRIVATE STUDENTS

BY

A. M. KELLAS, B.Sc. (LOND.), PH.D. (HEIDELBERG)

LECTURER ON CHEMISTRY AT THE MIDDLESEX HOSPITAL MEDICAL SCHOOL  
FORMERLY EXAMINER IN CHEMISTRY TO THE CONJOINT BOARD  
OF THE ROYAL COLLEGES OF PHYSICIANS AND SURGEONS

LONDON

HENRY FROWDE  
OXFORD UNIVERSITY PRESS

HODDER & STOUGHTON  
WARWICK SQUARE, E.C.

1909  
R



QD45  
K29  
1909

## PREFACE

ONE has been accustomed to hear the reproach flung at the teaching of Practical Chemistry that the student often carries out his analysis as a routine, and rarely seems to appreciate that the subject should be studied closely in connexion with his theoretical work, in the assimilation of which it should be of great assistance. After nearly seventeen years' experience in teaching medical students, the author has come to the conclusion that an elementary practical book should contain more complete explanations than are usually given, and that the work should be taken in the same order, and in some respects more closely correlated to the theoretical part of the science than is generally the case. The author is of the opinion that Chemical Analysis, carried out intelligently and coupled with the writing of equations expressing the positive reactions, is of considerable educational value.

The present manual has been designed to thoroughly cover the requirements of candidates preparing for the examination of the Conjoint Boards of the Royal Colleges of Physicians and Surgeons, but it is believed that the work will supply what is required by Science and Higher Grade Schools as well as by the private student. The theoretical portions will perhaps be found more complete and systematic than usual, which it is hoped will prove advantageous. The Lists of Common Compounds of the respective Metals given opposite each Summary of Tests is a novelty which should be found useful.

If time does not allow of complete treatment many of the experiments of Part I might be omitted, provided that the student attends a course of lectures.

Any suggestions from teachers regarding arrangement or matter will be thankfully received and carefully considered by the author.

A. M. KELLAS.

CHEMICAL DEPARTMENT,  
MIDDLESEX HOSPITAL MEDICAL SCHOOL,  
LONDON, W.

# CONTENTS

## PART I

PAGE

### SIMPLE PREPARATIONS OF NON-METALLIC ELEMENTS AND COMPOUNDS . . . . . 3-44

Introduction—Preliminary Notes on Chemical Theory, 3. The Common Valencies of the Elements, 5. General Manipulations in connexion with the setting up of Apparatus: I. Setting up of Apparatus, 8. II. General Experimental Processes; Solution, Filtration, Evaporation, Crystallization, Distillation, Sublimation, 10. Exercise involving Filtration, Evaporation, and Crystallization, 12. Preparation of Hydrogen, 14. Oxygen, 17. Calculations of Weights of Reacting Substances and of Products of Reaction from Equations; Estimation of the Volume of Gaseous Bodies, 21. Calculation of Volume from Weight, 22. Nitrogen, 26. The Atmosphere, 27. Ammonia, 28. Oxides of Nitrogen, 30. Nitric Acid, 32. The Halogen Elements, 34. The Halogen Hydracids, 36. The Oxides of Carbon, 38. Oxides of Sulphur, 41. Sulphuric Acid, 42. Compounds of Phosphorus, 43.

## PART II

### PREPARATION OF TYPICAL COMPOUNDS OF THE METALS . . . . . 49-70

A. Preparation of Metallic Salts, 49. Potassium Nitrate, 57. Barium Nitrate, 58. Lead Nitrate, 59. Lead Iodide, 60. Ammonium Chloride, 61. Copper Sulphate, 61. Ferrous Sulphate, 62.

Organic Compounds: (1) Lead Acetate, 63. (2) Ammonium Oxalate, 63. (3) Potassium Hydrogen Tartrate, 64. (4) Potassium Antimonyl Tartrate, 64.

Additional Preparations: Sodium Sulphate, 65. Disodium Hydrogen Phosphate, 65. Sodium Pyroborate, 65. Sodium Bicarbonate and Sodium Carbonate, 65. Potassium Bromide, 66. Mercuric Iodide, 67. Cuprous Chloride, 67. Potash Alum, 68.

B. Preparation of a few Typical Oxides: Ferric Oxide, 68. Mercuric Oxide, 68. Cupric Oxide, 69. Cuprous Oxide, 69.

Preparation of Hydroxides: (1) Sodium Hydroxide, 69. (2) Lead Hydroxide, 70. (3) Copper Hydroxide, 70. (4) Bismuth Hydroxide, 70. (5) Zinc Hydroxide, 70. (6) Ferric Hydroxide, 70. (7) Aluminium Hydroxide, 70. (8) Calcium Hydroxide, 70.

## PART III

	PAGE
<b>TESTS FOR ELECTRO-POSITIVE RADICLES . . . .</b>	<b>75-179</b>

Detection of the Metals—the Electro-positive Radicles or Kations, 75.

A. Dry Tests for the Metals, 80. (1) Reduction on Charcoal, 84. (2) Coloured Masses, 85. (3) Coloured Incrustations around the Heated Area, 86. (4) Borax Bead Tests, 86. (5) Platinum Wire Tests, 87.

B. Wet Tests for the Metals, 89. List of Reagents, 93. Lists of Tests, 94-138. Analytical Tables based upon the foregoing Lists of Tests, 139. The Arrangement of the Metals into Groups, 141. A. Analysis of any given Aqueous Solution of a Simple Substance for a Single Metallic Radicle, 144. B. Analysis of a Simple Substance given in the Solid State, 157. C. Analysis of a Solution containing Two or more Metals belonging to Different Analytical Groups, 162. D. Analysis of a Solid Mixture containing Two or more Metals belonging to Different Analytical Groups, 167. E. Summary of Analysis of a Mixture, given in Solution or in Solid State, containing Two or more Metals which may belong to the same Group, 169. F. Noteworthy Substances, many of which are of Characteristic Appearance, and some of which are difficultly soluble or insoluble, 171. Identification and Separation of Metals of Group I, 173. Identification and Separation of Metals of Group II, 174.

## PART IV

<b>A. IDENTIFICATION OF ACID RADICLES . . . .</b>	<b>184-209</b>
---------------------------------------------------	----------------

List of Acids, 185. Tables of Solubility, 186. Summary of Tests for Acid Radicles, 190. Reactions of Salts of the Acids, with Tests for Free Acids, where met with, 190. Detection of Acids, 206.

<b>B. IDENTIFICATION OF METALLIC OXIDES AND HYDROXIDES . . . . .</b>	<b>210-212</b>
----------------------------------------------------------------------	----------------

Complete Summary of Method of Procedure in carrying out Tests for Acid Radicles and for Soluble Metallic Hydroxides . . . . 213-217

## PART V

<b>QUANTITATIVE ANALYSIS . . . . .</b>	<b>223-249</b>
----------------------------------------	----------------

A. Gravimetric Analysis, 223. B. Volumetric Analysis, 230. Acidimetry and Alkalimetry, 234. Method of determining the Strength of a Solution of Acid or Alkali, given a Solution of known Strength, 236. Method of Procedure in above Case, 237. Method of calculating Results of Experiments, 239. Estimation of Oxalic Acid by means of Standard Potassium Permanganate, 246. Estimation of Chlorides volumetrically by Standard Silver Nitrate, using Potassium Chromate as Indicator, 249.

<b>Weights and Measures—Imperial (or British) and Metric Systems . .</b>	<b>250</b>
--------------------------------------------------------------------------	------------

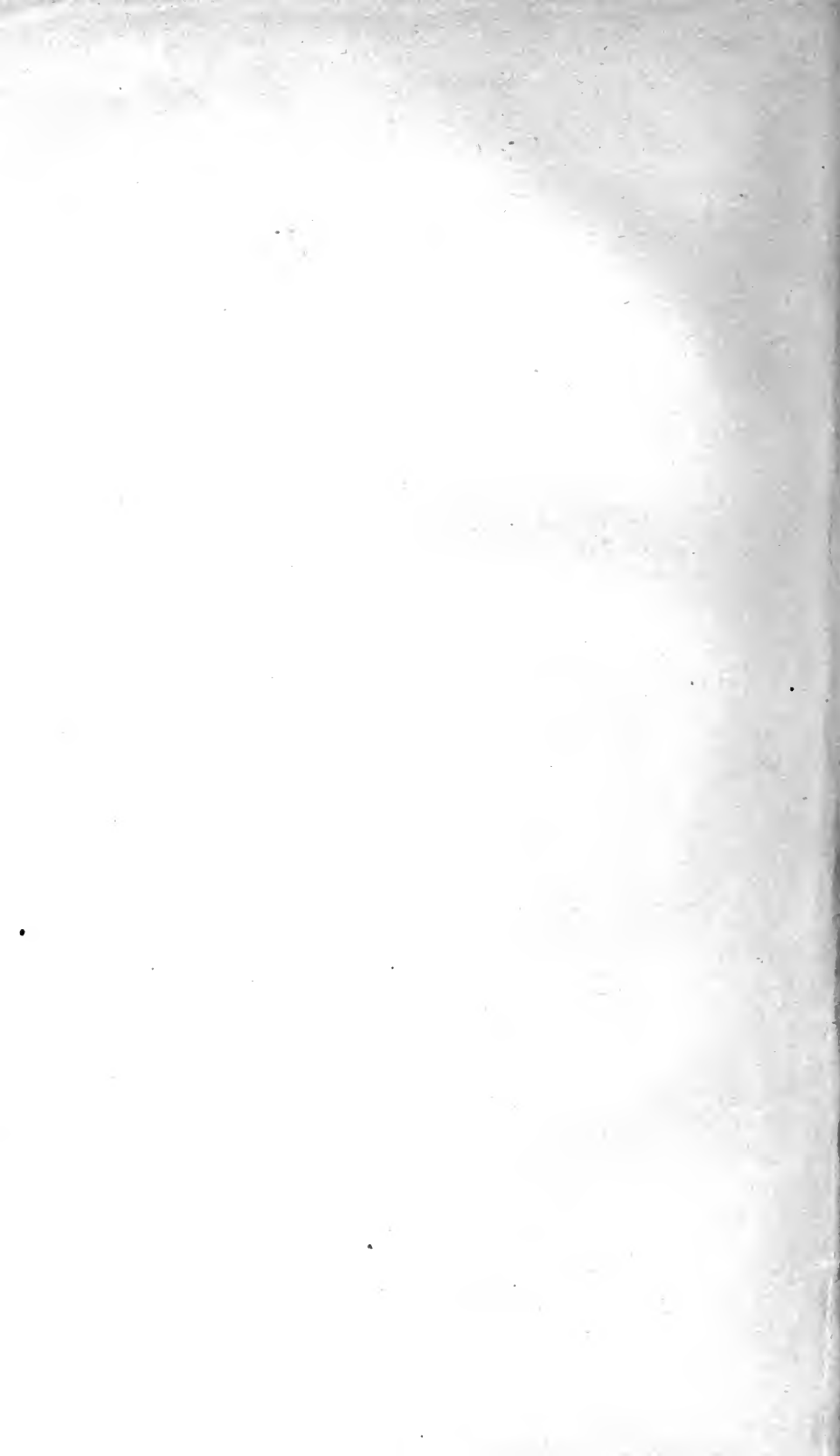
<b>Table of Atomic Weights (1909) . . . . .</b>	<b>251</b>
-------------------------------------------------	------------

<b>INDEX . . . . .</b>	<b>257</b>
------------------------	------------



## PART I

### SIMPLE PREPARATIONS OF NON-METALLIC ELEMENTS AND COMPOUNDS



# INTRODUCTION TO PRACTICAL CHEMISTRY

## PART I

### SIMPLE PREPARATIONS OF NON-METALLIC ELEMENTS AND COMPOUNDS

#### INTRODUCTION

##### PRELIMINARY NOTES ON CHEMICAL THEORY

THE student will have already learned that all bodies may be referred to one of three classes, viz. :—**Elements**, **Compounds**, or **Mixtures**.

**DEFINITION.** An **Element** is a body which so far as we know cannot by ordinary means be split up into simpler bodies, e. g. oxygen, silver, arsenic.

**DEFINITION.** A **Compound** is formed by the union of two or more elements in fixed definite proportions by weight, e. g. water, hydrochloric acid.

**DEFINITION.** **Mixtures** may consist of mixtures of elements, mixtures of compounds, or mixtures of elements and compounds in any proportion by weight; e. g. ordinary black gunpowder is a mixture of carbon, sulphur, and potassium nitrate (nitre) in proportions which may vary within considerable limits, and mixtures of the constituents might be made in any proportion whatever.

One generally starts the study of Chemistry with a consideration of the elements known as the '**non-metals**', and the more important compounds of these elements with hydrogen and oxygen.

The elements are for convenience divided into two great groups, the **Non-metals** and the **Metals**, and there is a small sub-group—the **Metalloids**. The distinctions between these groups depend essentially upon chemical relationships, and

## 4 SIMPLE PREPARATIONS OF NON-METALLIC

cannot be profitably considered until later, when the more important types of compounds concerned in the distinctions will have been met with.

The following are the chief elements which, along with their compounds, are generally dealt with in an elementary course, and will be considered here:—

### I. NON-METALS. II. METALLOIDS. III. METALS.

ELEMENT.	SYMBOL.	ELEMENT.	SYMBOL.	ELEMENT.	SYMBOL.
Hydrogen	H	Arsenic	As	Silver	Ag
Oxygen	O	Antimony	Sb	Mercury	Hg
Nitrogen	N	2		Lead	Pb
Phosphorus	P			Copper	Cu
Chlorine	Cl			Bismuth	Bi
Bromine	Br			Tin	Sn
Iodine	I			Aluminium	Al
Carbon	C			Chromium	Cr
Sulphur	S			Iron	Fe
Silicon	Si			Zinc	Zn
Boron	B			Manganese	Mn
	11			Barium	Ba
				Strontium	Sr
				Calcium	Ca
				Magnesium	Mg
				Sodium	Na
				Potassium	K
				17	

We are therefore concerned with only 30 out of the 81 known elements. A complete list of elements with their atomic weights is given at the end of this book (p. 251).

The student should refer to his theoretical book for complete explanations regarding fundamental terms such as atom, molecule, valency, &c., but the following summary may prove useful:—

**DEFINITION.** An **atom** is the smallest portion of an element which can enter into chemical combination, e.g. H stands for an atom of hydrogen.

**DEFINITION.** A **molecule** is the smallest portion of an element or compound which can exist in the free state, e.g. H<sub>2</sub> stands for a molecule of hydrogen, there being 2 atoms in a molecule of that element.

**Formulae. Equations. Valency.**

To be able to understand and write chemical formulae and equations is of fundamental importance in both practical and theoretical chemistry. The student should therefore spare no trouble to acquire a knowledge of the principles upon which the writing of equations is based. If he does not comprehend the following explanations on a first perusal, he should return to them again and again until he does so.

**Formulae** are used to represent molecules of substances, and indicate the relative number of atoms of each element present, e.g.  $\text{H}_2\text{O}$  represents a molecule of water, and shows that the molecule consists of 2 atoms of hydrogen combined with one of oxygen. In **chemical equations** one generally indicates the decomposition of the molecules of a body, or the interaction of molecules of different substances. Before one can write equations one must therefore be able to write formulae representing molecules, and before molecules can be correctly rendered, what is termed the **valency** of the different elements must be known.

**DEFINITION.** The **Valency** of an element expresses the number of hydrogen atoms (or the equivalent of hydrogen) which one atom of the element can combine with or replace.

Elements are classed as **monovalent**, **divalent**, **trivalent**, &c., the prefix indicating the number of hydrogen atoms which one atom of the element can combine with or replace. The valency of an element is frequently variable, especially in the case of the non-metals, and it is therefore inadvisable that the beginner should spend too much time upon attempts to fully understand all the equations in the following preparations of non-metallic elements and compounds. When he comes to the preparation of metallic salts, however, he should be able in most cases to balance up the equations from the following valency table.

**THE COMMON VALENCIES OF THE ELEMENTS.**

<b>Monovalent Elements</b>	H, Cl, Br, I, Na, K, $(\text{NH}_4)^*$ , Ag, $\text{Cu}^{\text{ous}}$ , $\text{Hg}^{\text{ous}}$ .
<b>Divalent</b>	„ O, $\text{S}^{\text{II}}$ , Mg, Ca, Sr, Ba, Zn, $\text{Mn}^{\text{ous}}$ , $\text{Fe}^{\text{ous}}$ , Pb, $\text{Sn}^{\text{ous}}$ , $\text{Cu}^{\text{ic}}$ .
<b>Trivalent</b>	„ N, B, P, As, Sb, Bi, $\text{Fe}^{\text{ic}}$ , Al, Cr.
<b>Tetravalent</b>	„ C, Si, $\text{S}^{\text{IV}}$ , $\text{Sn}^{\text{ic}}$ .
<b>Pentavalent</b>	„ N, P, As, Sb, Bi.
<b>Hexavalent</b>	„ $\text{S}^{\text{VI}}$ .

\* The Ammonium Group  $(\text{NH}_4)$  behaves like a monovalent metal.

## 6 SIMPLE PREPARATIONS OF NON-METALLIC

The full significance of this table will not be appreciated by the beginner until he comes to write the equations expressing the reactions which he carries out while testing for metals and acids. To enable the student to appreciate the general application of the table for the writing of formulae and equations, one must anticipate the definitions for acids and salts which are more fully explained later on.

**Acids** are compounds containing hydrogen which can be replaced by a metal, and **Salts** are the compounds formed from acids by replacement of part or all the replaceable hydrogen by metal.

Consider first of all the salts termed **chlorides** which are derived from **hydrochloric acid**,  $\text{HCl}$ .

The formulae for the chlorides of the **monovalent elements** would be derived from one molecule of acid by replacing the hydrogen atom by an atom of metal, and would be:— $\text{NaCl}$ ,  $\text{KCl}$ ,  $(\text{NH}_4)\text{Cl}$ ,  $\text{AgCl}$ ,  $\text{HgCl}$  (mercurous chloride),  $\text{CuCl}$  (cuprous chloride).

The formulae for the **chlorides of the divalent elements** must be obtained by replacement of 2 atoms of hydrogen by 1 of metal. This obviously requires that the hydrogen of 2 molecules of hydrochloric acid be replaced, since one molecule of hydrochloric acid contains only one atom of hydrogen. One would obtain in this way the formulae:— $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{FeCl}_2$  (ferrous chloride),  $\text{PbCl}_2$ ,  $\text{SnCl}_2$  (stannous chloride),  $\text{CuCl}_2$  (cupric chloride). In the case of the **trivalent elements** the formulae would be obtained by replacing the hydrogen of three molecules of hydrochloric acid by one of metal:— $\text{AsCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{BiCl}_3$ ,  $\text{FeCl}_3$  (ferric chloride),  $\text{AlCl}_3$ ,  $\text{CrCl}_3$ .

As regards **tetravalent elements**, such as tin in the stannic condition, the formula would be derived from  $4\text{HCl}$  by replacing 4 atoms of hydrogen by one atom of metal, the formula for stannic chloride being  $\text{SnCl}_4$ .

Consider next the salts of nitric acid,  $\text{H—NO}_3$ , known as the **nitrates**. In writing the formulae for the nitrates one has merely to concentrate attention upon the valency of the elements because the radicle  $\text{—NO}_3$  remains intact. The formulae for the nitrates may therefore be similarly derived to those of the chlorides, and if one substitutes an  $\text{—NO}_3$  group for each chlorine atom in the above list of chlorides, the correct formulae for the nitrates will be obtained:—

**Nitrates of monovalent metals.**  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{AgNO}_3$ ,  $\text{HgNO}_3$ . (Cuprous nitrate is not met with.)

**Nitrates of divalent metals.**  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Sn}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ .

**Nitrates of trivalent metals.**  $\text{Bi}(\text{NO}_3)_3$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Al}(\text{NO}_3)_3$ . Arsenic and antimony nitrates are not known.

The formulae of the sulphates, as the salts of sulphuric acid are called, are not similar to those of the chlorides and nitrates, because sulphuric acid ( $\text{H}_2\text{SO}_4$ ) has two atoms of displaceable hydrogen in the molecule. In the case of sodium, potassium, and ammonium two sulphates are met with in each case, namely the acid salts or bisulphates where only one atom of hydrogen has been replaced, and the normal sulphates where both hydrogen atoms have been displaced by metal.

### 1. Sulphates of monovalent metals.

(a) Bisulphates.  $\text{NaHSO}_4$ ,  $\text{KHSO}_4$ ,  $(\text{NH}_4)\text{HSO}_4$ .

(b) Normal sulphates.  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Ag}_2\text{SO}_4$ ,  $\text{Hg}_2\text{SO}_4$ . (Cuprous sulphate is not known.)

**2. Sulphates of divalent metals.**  $\text{MgSO}_4$ ,  $\text{CaSO}_4$ ,  $\text{BaSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{MnSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{CuSO}_4$ . Here both atoms of hydrogen in  $\text{H}_2\text{SO}_4$  are replaced by one atom of metal.

**3. The formulae for the sulphates of trivalent metals** can be deduced in the following way: One molecule of sulphuric acid contains only 2 atoms of hydrogen, and therefore an insufficient number for replacement by one atom of a trivalent element. Two molecules of sulphuric acid ( $2\text{H}_2\text{SO}_4$ ) contain 4 atoms of hydrogen, and 4 atoms of a monovalent element could not be replaced without remainder by atoms of a trivalent element. Three molecules of sulphuric acid, however ( $3\text{H}_2\text{SO}_4$ ), contain 6 atoms of hydrogen, and 2 atoms of a trivalent element could exactly replace these 6 atoms. The formulae would therefore be:— $\text{Bi}_2(\text{SO}_4)_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{Cr}_2(\text{SO}_4)_3$ .

Other formulae would be analogous. It is worth noting, for example, that the formulae for the oxides and sulphides which might be represented as if derived from  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  respectively would in most cases be exactly similar to those of the sulphates: one has merely to put  $-\text{O}$  or  $-\text{S}$  for  $-\text{SO}_4$  in above formulae, e.g. zinc oxide has the formulae  $\text{ZnO}$ , and zinc sulphide is  $\text{ZnS}$ , corresponding to zinc sulphate,  $\text{ZnSO}_4$ .

## 8 SIMPLE PREPARATIONS OF NON-METALLIC

### GENERAL MANIPULATIONS IN CONNEXION WITH THE SETTING UP OF APPARATUS. GENERAL EXPERIMENTAL PROCESSES.

Before going on to consider the preparation and important reactions of the non-metals and their compounds, the general manipulations required in the setting up of apparatus, and also a few general experimental processes, must be considered.

**Apparatus required:**—Flasks of various types, round bottomed, flat bottomed and conical, glass tubing of moderate bore—say 3–5 millimetres internal diameter, retorts, filter funnels, test-tubes, porcelain basins, corks (and cork-pressers), triangular and round files, wire gauze, retort stand, condenser, rubber tubing.

#### I. SETTING UP OF APPARATUS.

The cutting and bending of glass tubes and boring of corks are general operations which have to be performed in setting up apparatus.

The proper method of cutting a glass tube is as follows:—Place the tube horizontally on the bench and make a mark with a triangular file at the point where the glass is to be broken. Take the tube in both hands, but mainly gripped between the thumb and first fingers of each hand. The backs of the hands should be outwards, and the thumbs should be directed towards each other and along the top of the tube. The file mark should be in the short space—say  $\frac{1}{4}$  to  $\frac{1}{2}$  inch—between the thumbs. On gripping firmly with the thumbs and pressing upwards and outwards with the fingers, the tube will usually break neatly at the file mark. The cut edges should always be rounded off by heating them in the Bunsen flame with constant rotation of the tube until the glass just fuses and forms a rounded surface.

**Bending of glass tubes.** The bending of tubes is generally carried out in the ordinary flat flame, and not with the Bunsen burner, the heat of which is too intense and localized for the purpose. Hold the tube along the top of the flat flame—which should be parallel to the operator's body—so that the point where the bend is to be made is at the middle of the heated area. Rotate the tube continually, and if the flame be small, move also slightly backwards and forwards so as to heat a fair length of tubing. When the glass has softened sufficiently withdraw from the flame and bend the tube as required while holding it at right angles to the face and on a level slightly below the eyes,



so that one can look along the top of the tube during the bending process.

**Cork-boring.** As a preliminary to boring, the cork selected should either be squeezed in a cork press or covered with paper (to keep it clean) and then well rolled under the foot so as to make it resilient. The cork is then carefully bored with the number of holes required, starting from the small end. The cork-borer used should always be of slightly smaller diameter than the end of the tube to be introduced. Moisten the cork-borer with alcohol (or water) and rotate it while forcing it through the cork. Until proficiency is attained it is usually a good plan to bore half-way from each end of the cork. During boring the cork-borer is moved horizontally, the cork being held in the hand. If the beginner finds it more convenient to hold the cork against a vertical body (e. g. the wall) while boring, care must be taken to finish the boring in the hand, otherwise the end of the cork-borer may be blunted. Steel cork-borers (which are the most satisfactory) must be carefully dried before being put away. After boring, the holes made may be smoothed and slightly enlarged if necessary by means of the round file.

**EXERCISE.** To fit up a wash bottle.

A convenient wash bottle for students' use consists of a half litre flat-bottomed or conical flask of moderately stout glass fitted with a doubly bored cork. Through one opening of the cork passes a short tube bent up at an angle of about  $65^\circ$  to the horizontal from a point two or three inches above the cork, and projecting only a short distance into the flask. Through the other hole passes a tube which should reach down to near the bottom of the flask, and be bent round to make an angle of about  $35^\circ$ , so that by proper adjustment the bent part of the two tubes will be in one oblique line as indicated in Fig. 1.

A few inches below the bend the tube is either drawn out to form a jet, or is cut off and connected to a small jet by means of rubber tubing. The latter is the more convenient arrangement and is the one represented in the ordinary flask in Fig. 1.

**To make a jet** take a short length of tubing and heat the central portion in the Bunsen flame with constant rotation. When the glass is soft remove from the flame and push gently from the two ends towards the centre. If necessary repeat until the central portion of the tube is considerably thickened. Turn down the flame until only the thickened portion is heated,

## 10 SIMPLE PREPARATIONS OF NON-METALLIC

rotating as usual, and when quite soft remove from the flame and draw out steadily with constant rotation so as to increase the length of the tube two or three inches. On making a file mark near the centre and breaking two jets would be obtained. Cautiously round the ends of one jet in the Bunsen flame, but do not overheat or the opening may close up.

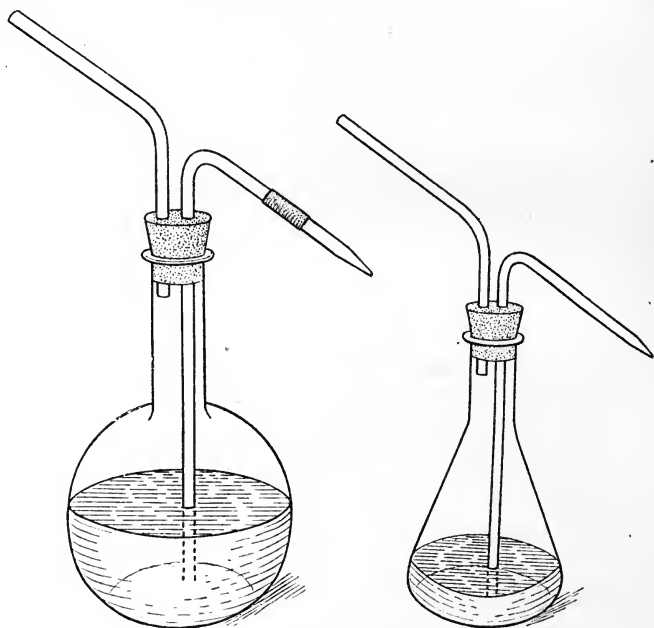


FIG. 1. WASH BOTTLES.

In putting glass tubes into cork or rubber stoppers it is well to moisten the tubes and insert them by a gentle turning motion. [Caution. Tubes may break and cut the hands seriously on attempting to force them carelessly through corks.]

### II. GENERAL EXPERIMENTAL PROCESSES. SOLUTION, FILTRATION, EVAPORATION, CRYSTALLIZATION, DISTILLATION, SUBLIMATION.

One of the commonest operations carried out in chemistry is the preparation of a solution.

**DEFINITION.** A solution is a homogeneous mixture which cannot be split into its constituent parts by mechanical means.

Many types of solution are met with, such as solutions of solids in liquids, e. g. potassium nitrate (nitre) or sugar in water, of liquids in liquids, e. g. alcohol and water, and of gases in liquids, e. g. hydrochloric acid gas in water.

The liquid in which the solution is formed is termed the **solvent**, and a body dissolving in the liquid is said to be **soluble** and is called the **solute**.

**The factors determining the solubility of a solid or liquid in a liquid are:—**(1) the solvent employed, (2) the substance, (3) the temperature. The solubility as a rule increases with temperature. For any particular temperature there is a certain maximum quantity of solute which can be dissolved by a solvent, and when this quantity is present, the solution is said to be saturated. A saturated solution will not take up more of a solid or liquid when the solution is in direct contact with it. If the quantity of solid or liquid dissolved in a liquid is stated, the amount is generally expressed in grams for a certain volume of solution, e. g. grams per litre, or as a percentage.

In the case of **gases** four factors condition solubility, viz. :—(1) solvent, (2) gas considered, (3) temperature, (4) pressure. In the case of gases the solubility diminishes with rise of temperature, and as regards pressure a definite law can be given generally called **Henry's Law**. The solubility of a gas varies directly as the pressure at which solution takes place, provided the volume of gas is always measured at standard temperature and pressure. The solubility is generally expressed as a coefficient.

**DEFINITION.** The **coefficient of solubility** of a gas is the volume of gas soluble in one volume of solvent at normal temperature and pressure (i. e. at  $0^{\circ}\text{C}$ . and 760 mm.), e. g. the coefficient of solubility of ammonia is 1140, of hydrochloric acid 540, of sulphur dioxide 80, of sulphuretted hydrogen 4.5, of carbon dioxide 1.8, of nitrous oxide 1.3, of oxygen 0.04, of nitrogen 0.02, and of hydrogen 0.017. Coefficients of solubility may be stated for other temperatures, e. g. at  $15^{\circ}\text{C}$ . the coefficient for ammonia is 750 and for hydrochloric acid 450.

We are generally concerned in elementary analysis with solutions of solids in liquids, and a common operation which has to be effected is the separation of a soluble body from one insoluble in the particular solvent dealt with. An example of this type of operation is worth working out in detail.

## 12 SIMPLE PREPARATIONS OF NON-METALLIC

### EXERCISE INVOLVING FILTRATION, EVAPORATION, AND CRYSTALLIZATION.

Make a mixture of about 5 grams of potassium nitrate and 5 grams of sand. Warm the mixture in a basin with 30-40 c.c. of water: the nitre will dissolve. Fold a round filter paper of say 3 to 5 inches diameter first along a diameter and then at right angles so as to form a quadrant of a circle. It will be found that

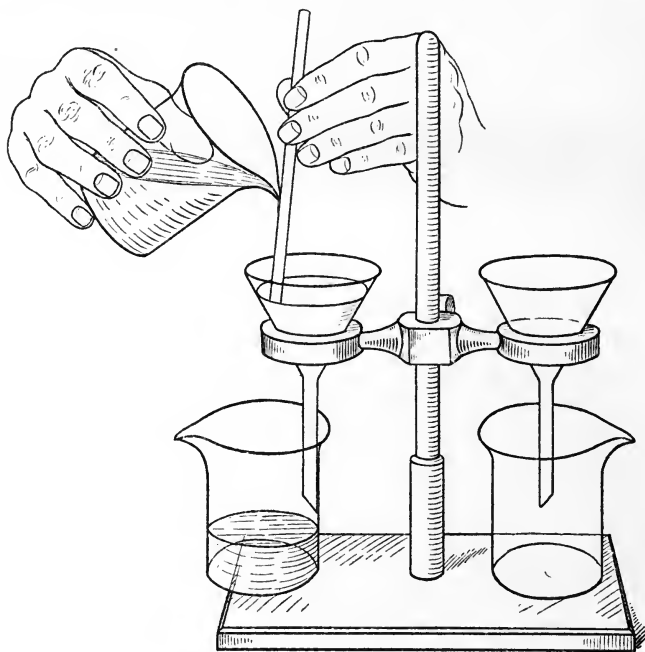


FIG. 2. FILTRATION. Showing how to avoid loss of Material.

the paper can be opened from either side to form a hollow cone. Open the paper in a cone, place in a filter funnel, moisten with water, press the paper against the sides of the funnel so as to make it fit tightly, put a porcelain dish under the funnel and separate the solution of nitre from the insoluble sand by slowly pouring the whole of the contents of the beaker into the funnel, taking care not to quite fill the cone at any moment. The solution should be poured from the beaker into the funnel along a glass rod as indicated in Fig. 2. The liquid which passes through the porous paper into the dish is called the *filtrate*, and

the sand remaining on the filter paper is called the **residue**. The process is termed **filtration**.

Wash the residue and filter paper quite free from nitre by a jet of water from the wash bottle, filling the filter paper two or three separate times, and directing the jet at first so as to strike above the top of the filter paper, and then gradually lowering it. In this way the residue of sand will be washed into the apex of the filter cone, and this is the general method of washing residues free from traces of adhering solution. The solution obtained in the dish may be evaporated down to crystallization. By evaporating down at a temperature near the boiling point, the liquid can

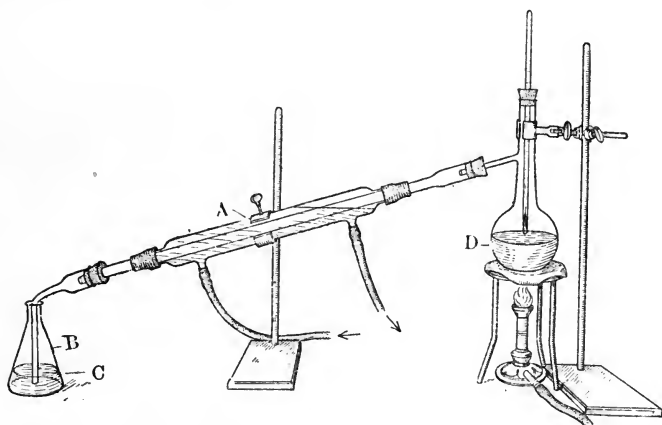


FIG. 3. DISTILLATION. A, Condenser; B, Receiver; C, Distillate; D, Distilling flask.

be brought into a state of saturation at that temperature, and crystals will begin to separate. If the liquid be now allowed to cool to room temperature a large quantity of the solid will separate, because the quantity of nitre required to saturate water at room temperature (say  $20^{\circ}\text{C}.$ ) is much less than that required to saturate water boiling about  $100^{\circ}\text{C}.$

Sometimes the solvent may be required as well as the solute. In such a case the process of distillation must be effected.

**DEFINITION.** Distillation means the conversion of a liquid into vapour and condensation into liquid in another vessel.

Place in a distilling flask of capacity 100 c.c. about 50 c.c. of tap water, add a few cubic centimetres of potassium permanganate solution, connect with a condenser and receiver and carry out

## 14 SIMPLE PREPARATIONS OF NON-METALLIC

a distillation by heating the flask containing the liquid with a Bunsen flame. The flask should be placed over wire gauze as shown in Fig. 3.

Add a few small pieces of unglazed porcelain to the liquid before distilling to prevent the temperature rising above the true boiling point (super-heating) and consequent irregular boiling. The condenser consists essentially of an inner tube which is connected to the side tube of the distilling flask, and an outer tube through which cold water is circulated. The water on heating vaporizes, and the vapour passing into the cooled condenser tube changes to the liquid state and runs into the receiver. Pure water distils over; this can readily be proved by evaporating a small quantity to dryness on a watch-glass, or by determining either of two important physical constants of the liquid, viz. the boiling-point or the freezing-point. Pure water boils at  $100^{\circ}\text{C}$ . and freezes at  $0^{\circ}\text{C}$ .

**Sublimation** is another general operation, worth mentioning here, by which separation of substances can be effected.

**DEFINITION.** **Sublimation** means the conversion of a solid into vapour and recondensation of the vapour in another portion of the apparatus.

**EXERCISE.** As a practical instance of separation by sublimation make a mixture of about a gram of common salt and a gram of ammonium chloride (sal ammoniac), place in a dry test-tube, and heat cautiously with a Bunsen flame. The ammonium chloride sublimes and condenses on the cool upper portion of the tube. Ammonium, mercury, arsenic, and antimony compounds can sometimes be separated from non-volatile bodies in this way.

### PREPARATION OF HYDROGEN. SYMBOL H.

Atomic weight 1. Density 1.

[**Caution.** Hydrogen forms an explosive mixture with air.]

#### **From Zinc and dilute Sulphuric Acid.**

(a) Place in a dry test-tube a few pieces of granulated zinc, and then add about 1 c.c. of concentrated sulphuric acid. Note that practically no action occurs. On heating, a gas is evolved which has a strong odour of burning sulphur. This gas is sulphur dioxide.

(b) Add slowly with constant shaking about 5 c.c. of concentrated sulphuric acid to about 30-40 c.c. of water. [**Caution.** Do

not add the water to the acid.] Pour the solution on to a few grams of granulated zinc in a test-tube, small flask, or Woulff's bottle. Close the vessel by means of a cork (preferably of rubber) carrying a thistle funnel and delivery tube, the end of which should be placed under water in a trough as indicated in Fig. 4. After allowing time for the air to be displaced collect some of the gas in small jars or test-tubes, and carry out the following tests:—

(1) If a jar is used close it by means of a ground glass plate the rim of which has been lightly smeared with vaseline, if a test-

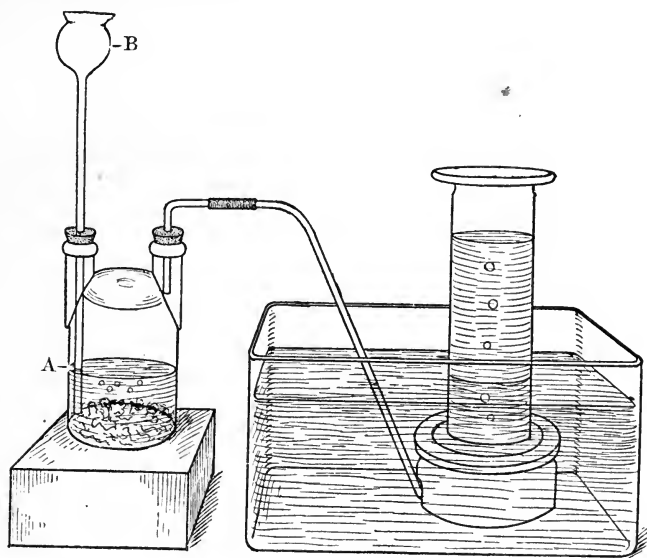


FIG. 4. PREPARATION OF HYDROGEN. A. Woulff's bottle; B, Thistle funnel.

tube is used close with the thumb, and, keeping the jar or tube inverted, apply a lighted match or taper to the mouth. The gas burns with an almost non-luminous flame. On putting the lighted match or taper up into the vessel it will be extinguished. This experiment shows that hydrogen burns in air, but does not allow carbonaceous material such as wood or wax to burn in it. The gas is said to be combustible, but not to support combustion. **Combustion** in chemistry generally means chemical action attended by the evolution of light and heat.

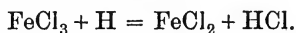
(2) Place a tube filled with gas with the mouth upwards, remove the cover from the mouth, and after about a second apply

## 16 SIMPLE PREPARATIONS OF NON-METALLIC

a light. A sharp explosion is heard, and a flash of light passes down the tube.

(3) Remove the delivery tube from the trough and attach by means of a short piece of rubber tubing a small jet, preferably made of hard glass. Before attaching the jet place in the tube near the wide end a loose plug of cotton-wool, which will to a considerable extent obviate the risk of explosion if the hydrogen issuing from the jet is ignited before the air has been completely displaced from the vessel. Add more zinc and dilute sulphuric acid if necessary, and when the reaction has been proceeding vigorously for a few minutes apply a light to the jet. The hydrogen will take fire and burn with a nearly non-luminous flame. (Note. If the jet is made of soft glass the flame will become yellow after a time because a trace of sodium will get into the flame from the glass.) Bring quickly over the burning jet a clean dry beaker, and hold it there for a few seconds. Note that the interior of the beaker becomes dimmed by the deposition of a film of moisture by condensation of the product of combustion of the hydrogen. Water is therefore formed when hydrogen burns in air.

(4) Pass hydrogen for a short time through a solution of ferric chloride to which sulphuric or hydrochloric acid has been added. No effect will be observed; the yellow colour of the solution remains unchanged. Now add a few pieces of granulated zinc to the liquid so as to set free hydrogen in the solution. In a few minutes the solution becomes practically colourless. The **nascent hydrogen**, as hydrogen just being liberated is termed, has reacted differently from ordinary hydrogen. It is assumed that ordinary hydrogen consists of molecules formed by the union of 2 atoms, represented by  $H_2$ , whereas nascent hydrogen consists of free atoms. The above reaction, which is a reduction process, would be represented by the equation

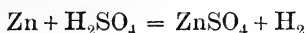


(5) The student should convince himself, either by direct experiment or by observation, that hydrogen can be readily obtained by other methods of preparation, e. g. the action of dilute sulphuric acid upon iron, action of hydrochloric acid upon zinc, iron or tin, or action of zinc upon strong caustic soda solution. It cannot be obtained by the action of nitric acid upon these metals. A test-tube provided with a cork and jet for igniting the hydrogen can be used for these methods of preparation.

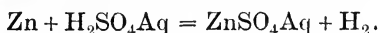


**Summary of what may be learnt from foregoing experiments.**

(1) Hydrogen can be prepared by the action of dilute sulphuric acid upon zinc, but not by the action of the concentrated acid, which gives chiefly sulphur dioxide. The equation



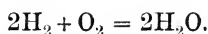
must therefore be wrong. If one represents dilute sulphuric acid as  $\text{H}_2\text{SO}_4\text{Aq}$ , where Aq stands for an indefinite proportion of water (Latin *Aqua*), the correct equation would be as follows:—



**NOTE.** As a general rule it is always better to put Aq after substances which are dissolved in water, and this practice will be adhered to throughout this book.

(2) Hydrogen can be obtained by the action of dilute sulphuric acid or of hydrochloric acid on other metals, but not by the action of nitric acid.

(3) Hydrogen burns in air to form water. The reaction depends upon the oxygen present in air and might be represented by an equation—



(4) Hydrogen does not support combustion.

(5) A mixture of hydrogen with air explodes if heated.

[Note.—One might learn from this to be careful in applying a light to any mixture containing hydrogen and air; e. g. coal gas contains generally about 50 per cent. of hydrogen as well as other combustible gases, so that a light should not be brought near any large volume of coal gas admixed with air.]

**Test for hydrogen.** The gas burns with a nearly non-luminous flame. Water is the only product.

**NOTE.** Similar summaries are not given in the further experiments described. The student should make them for himself. To learn how to summarize the results of a series of experiments in a few words is an important method of learning any experimental science.

## OXYGEN. SYMBOL O. Atomic weight 16.

(Density, i. e. weight compared with hydrogen as unity = 16.)

Carry out the following experiments:—

(1) Take a few crystals of potassium chlorate ( $\text{KClO}_3$ ) and heat in a test-tube of hard glass. The crystals fuse at about  $360^\circ \text{C}$ .

## 18 SIMPLE PREPARATIONS OF NON-METALLIC

and the liquid slowly gives off oxygen. Close the tube loosely with the thumb while heating it, so as to allow for escape of displaced air, but prevent downward convection currents. When the tube may be supposed to be filled with the evolved gas remove the thumb and insert into the tube a glowing splint of wood. (A cedar splint is best for this purpose.) The splint glows more brightly, and then bursts into flame. This constitutes a test for oxygen, but it is not entirely reliable because nitrous oxide behaves similarly (cf. p. 30).

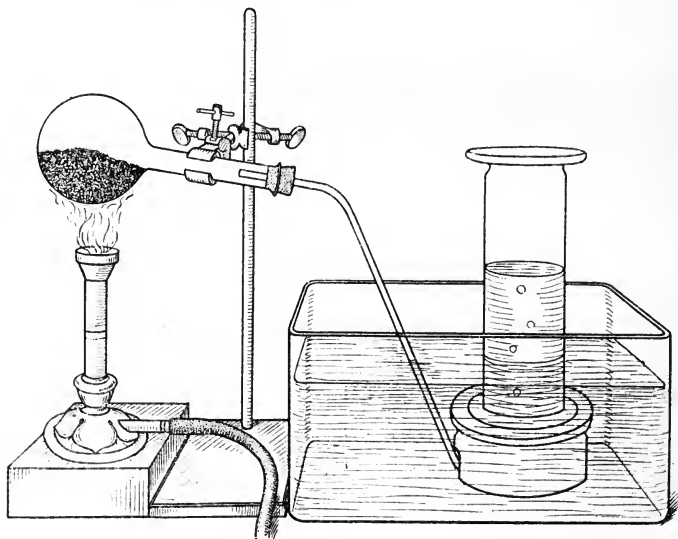


FIG. 5. PREPARATION OF OXYGEN.

(2) Put into a 6 to 8 oz. round-bottomed flask of hard glass a mixture of about one ounce of powdered potassium chlorate and two ounces of manganese dioxide. Connect with a delivery tube as shown in Fig. 5 and fill 4 small wide jars (or 8 ounce conical flasks) with the gas over water. If flasks are used they must be supported in position during the process of filling. [Caution. Be careful to heat very cautiously, otherwise the gas may come off so rapidly that the reaction flask will burst.] It will be noted during the experiment that the evolution of oxygen takes place at a much lower temperature in this second preparation although the manganese dioxide remains unaltered at the end. The manganese dioxide is called a 'catalytic agent'.

The glass jars should be closed by ground-glass plates slightly greased round the edges: it will be sufficient to close the flasks with ordinary rolled corks. The following reactions should then be carried out:—

(a) Heat in a deflagrating spoon in the Bunsen flame a small piece of carbon (e. g. wood charcoal) until it begins to glow at one point, and then rapidly place the spoon in one of the collection vessels. The ordinary deflagrating spoon consists of a shallow brass cup connected with a stout iron wire which passes through a cork in a brass disk. By pushing down or pulling up the wire one can adjust the position of the combustible body in the reaction vessel. [Note. If a deflagrating spoon is not available, one can easily be improvised from a piece of stout brass or copper wire and a piece of asbestos sheet. Bend the end of the wire into a small circle, and then fix into the ring a small cup made from the asbestos sheet. The end of the wire is then passed through a disk cut from the sheet or a piece of cardboard, and can be raised or lowered as required. The best position for the cup is near the bottom of the flask.] The product of combustion is a colourless gas, carbon dioxide (see p. 39).

Equation expressing the reaction  $C + O_2 = CO_2$ .

Add a small quantity of neutral litmus solution and shake the flask. The litmus turns red because of the formation of a solution of carbonic acid.

Equation  $CO_2 + H_2O + Aq = H_2CO_3Aq$ .

(b) Carry out a similar experiment with sulphur. The sulphur burns with a blue flame much more vigorously than in air, and a white fume fills the flask. The white fumes are due to a small quantity of sulphur trioxide ( $SO_3$ ), but the main product of the combustion is the colourless gas sulphur dioxide ( $SO_2$ ).

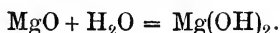
Equation  $S + O_2 = SO_2$ .

Add a few cubic centimetres of neutral litmus solution and shake the flask. The solution turns a bright red owing to the presence of sulphurous acid.

$SO_2 + H_2O + Aq = H_2SO_3Aq$ .

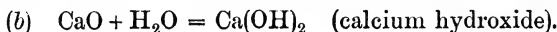
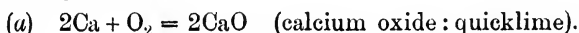
(c) Heat the end of a few inches of magnesium ribbon (or wire) held vertically by means of tongs in the Bunsen flame. When it begins to burn plunge into one of the vessels containing oxygen. A far more vigorous combustion takes place. Place the white product in a small flask, add a few cubic centimetres of

diluted red litmus solution—obtained by adding one drop of dilute hydrochloric acid to litmus solution—and warm gently on gauze over a flame. The litmus turns blue, owing to the presence of a slightly soluble base, magnesium hydroxide. The magnesium burns to form magnesium oxide. Equation  $2\text{Mg} + \text{O}_2 = 2\text{MgO}$ . The magnesium oxide takes up water to form magnesium hydroxide, which is slightly soluble in water.



Both magnesium oxide and magnesium hydroxide are 'bases'.

(d) Heat a small quantity of metallic calcium (raspings) in a clean deflagrating spoon until it begins to glow and then at once plunge into a vessel containing oxygen. The calcium glows more brightly and finally a white powder remains. After allowing to cool, wash the product off the spoon with water and add a few cubic centimetres of reddened litmus solution. The litmus will be turned blue because of the presence of a soluble base, calcium hydroxide.



In order that above reactions may be thoroughly understood, a few explanations must be given. On glancing at the equations expressing above combustions it will be observed that in each case the oxygen has combined with the element to form an **oxide**.

**DEFINITION.** An **Oxide** is a compound formed by the union of oxygen with another element.

The oxides form an important group of compounds, and there are several notable classes in the group. Two of the classes of oxides most commonly met with are the **Acid Anhydrides** and the **Basic Oxides**. The first and second products obtained in the above combustions (viz.  $\text{CO}_2$  and  $\text{SO}_2$ ) belong to the former group, and the third and fourth ( $\text{MgO}$  and  $\text{CaO}$ ) to the latter, and it should be noted that the above acid anhydrides are oxides of non-metals, while the basic oxides are oxides of metals.

**DEFINITION.** An **Acid Anhydride** is an oxide which when added to water forms an acid, e. g.  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$ . They are generally oxides of non-metals, but  $\text{CrO}_3$  (chromic anhydride) is a notable exception, being a metallic oxide which is an acid anhydride.

**DEFINITION.** A **Basic Oxide** is a compound of a metal with oxygen, which can react with acids to form a salt and water,

e. g.  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{BaO}$ ,  $\text{CuO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{HgO}$ ,  $\text{Ag}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ .

The basic oxides are invariably oxides of metals, and they belong to the group of substances called Bases.

Three fundamental groups of bodies have been mentioned in giving the above definitions, viz. **Acids**, **Bases**, and **Salts**. These may be defined as follows:—

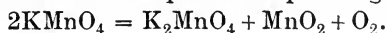
**DEFINITION.** An **Acid** is a compound containing hydrogen which can be wholly or partially replaced by a metal by the action of the acid on a moist metallic oxide or hydroxide, e. g.  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{CH}_3\cdot\text{COOH}$  (Acetic acid. Only one of the 4 hydrogen atoms is replaceable by metal).

**DEFINITION.** A **Base** is a metallic oxide or hydroxide, the metal in which can directly replace the hydrogen of an acid to form a salt and water, e. g. metallic oxides:  $\text{MgO}$ ,  $\text{CaO}$ .

Metallic hydroxides (compounds of a metal with oxygen and hydrogen):  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{Cu}(\text{OH})_2$ ,  $\text{Bi}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{AgOH}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ . The last two substances, which are very soluble in water compared with most of the other metallic hydroxides, are called *caustic alkalies*.

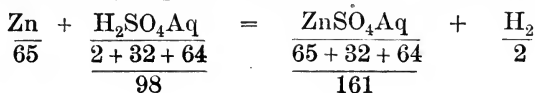
**DEFINITION.** A **Salt** is a compound derived from an acid by replacing part or all the replaceable hydrogen by metal. Most of the substances dealt with in qualitative analysis are salts, e. g.  $\text{NaCl}$ ,  $\text{KNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{CuCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{BaSO}_4$ .

**NOTE.**—Oxygen could be prepared by various other reactions, e. g. a good method is to heat potassium permanganate.



#### CALCULATIONS OF WEIGHTS OF REACTING SUBSTANCES AND OF PRODUCTS OF REACTION FROM EQUATIONS. ESTIMATION OF THE VOLUME OF GASEOUS BODIES.

In practical chemistry one has frequently to calculate the weights of bodies obtainable by reactions, and also weights of reacting substances; e. g. one might calculate what weight of anhydrous zinc sulphate could be obtained from say 130 grams of zinc, and also the weight of sulphuric acid required for the reaction. The equation expressing the relationship between the weights of zinc, sulphuric acid, and zinc sulphate would be



## 22 SIMPLE PREPARATIONS OF NON-METALLIC

It must be remembered in making calculations that the symbol for any element employed in an equation represents a number of parts by weight of the element corresponding to the atomic weight. Using the 'unitary' system of calculation one might proceed as follows:—

The equation shows that 65 parts by weight of zinc react with 98 parts by weight of sulphuric acid to yield 161 parts by weight of zinc sulphate.

∴ 65 grams of zinc react with 98 grams of  $\text{H}_2\text{SO}_4$  to yield 161 grams of zinc sulphate,

1 gram of zinc reacts with  $\frac{98}{65}$  grams of  $\text{H}_2\text{SO}_4$  to yield  $\frac{161}{65}$  grams of zinc sulphate,

and 130 grams of zinc react with  $\left(\frac{98}{65} \times \frac{2}{1}\right)$  grams  $\text{H}_2\text{SO}_4$  to

yield  $\left(\frac{161}{65} \times \frac{2}{1}\right)$  grams of zinc sulphate.

**Answer.** 130 grams of zinc would react with 196 grams of sulphuric acid and yield 322 grams of anhydrous zinc sulphate.

In the case of gases one may have to find not only the weight, but also the volume at a given temperature and pressure. e.g. Find the weight and volume of hydrogen obtained in above case, the temperature of collection being  $26^\circ\text{C}$ . and the pressure 690 millimetres.

The equation shows that

65 grams of zinc would by interaction with  $\text{H}_2\text{SO}_4$  yield 2 grams of hydrogen.

∴ 1 gram of zinc would by interaction with  $\text{H}_2\text{SO}_4$  yield  $\frac{2}{65}$  grams of hydrogen.

∴ 130 grams of zinc would by interaction with  $\text{H}_2\text{SO}_4$  yield  $\left(\frac{2}{65} \times 130\right)$  grams of hydrogen.

= 4 grams. **Ans.**

### CALCULATION OF VOLUME FROM WEIGHT.

There are two starting-points for calculating the volume of a gas from its weight.

**I. The molecular weight in grams of any gas occupies 22.25 litres at Normal Temperature and Pressure (termed N. T. P.); e. g. 2 grams of hydrogen ( $H_2$ ), 32 grams of oxygen ( $O_2$ ), 28 grams of nitrogen ( $N_2$ ), 44 grams of carbon dioxide ( $CO_2$ ) would each respectively occupy 22.25 litres at  $0^\circ C.$  and 760 mm. pressure.**

**II. The weight of one litre of Hydrogen (measured at N. T. P.) is 0.0899 gram. The weight of one litre of any other gas =  $0.0899 \times \text{density}$ , and the density of a gas is half its molecular weight,**

$$\therefore \text{The weight of one litre of any other gas} \\ = 0.0899 \times \frac{\text{molecular wt.}}{2}.$$

The first starting-point is generally the more convenient. In this case 2 grams of hydrogen occupy 22.25 litres at  $0^\circ C.$  and 760 mm.

$$\therefore 1 \text{ gram of hydrogen occupies } \frac{22.25}{2} \text{ litres at } 0^\circ C. \text{ and } 760 \text{ mm.}$$

$$\text{and 4 grams of hydrogen occupy } \left( \frac{22.25}{2} \times 4 \right) = 44.5 \text{ litres at N. T. P.}$$

Corrections must next be applied for pressure and temperature, which can be done by taking into consideration the laws expressing the relationship of volume to pressure and temperature respectively.

#### **A. Correct for Pressure.**

**Boyle's Law** states that the volume of a gas varies inversely as the pressure (temperature remaining constant), so that if the pressure is increased the volume is diminished, and vice versa. The standard pressure is 760 mm., and the pressure at collection 690 mm. At 690 mm. the volume will be greater than at 760 mm. in the ratio  $\frac{760}{690}$ . The volume of hydrogen collected at  $0^\circ C.$  and 690 mm. would be  $\left( 44.5 \times \frac{760}{690} \right)$  litres.

#### **B. Correct for Temperature.**

**Charles' Law.** The volume of a gas is directly proportional to its absolute temperature. **Absolute temperature =  $t^\circ C. + 273$ .**

The absolute temperature corresponding to  $0^\circ C.$  and to  $26^\circ C.$  would be 273 and  $(273 + 26)$ . The volume of gas at 299 absolute

## 24 SIMPLE PREPARATIONS OF NON-METALLIC

would be greater than the volume at 273 absolute, so that the volume of hydrogen at 690 mm. and 26° C. would be

$$44.5 \times \frac{760}{690} \times \frac{299}{273} = \left(44.5 \times \frac{76}{63}\right) \text{ litres.}$$

= 53.68 litres. **Answer.**

From this detailed explanation and example the following **general statement** may be deduced : To convert volume at N. T. P. (i.e. 0° C. and 760 mm.) into volume at any other temperature and pressure multiply by two factors, (a) by a factor expressing the ratio of the pressures, (b) by a factor expressing the ratio of the absolute temperatures.

The results might also be obtained from a formula, but it must be noted that it is not so satisfactory to apply a routine formula which might not be understood.

The formula would be

$$\frac{VP}{T} = \frac{V'P'}{T'},$$

where V, P, and T are the initial volume, pressure, and absolute temperature (T and P being in above case 0° C. and 760 mm.), and V', P', and T' the final volume, pressure, and absolute temperature. V' is required.

$$V' = V \times \frac{P}{P'} \times \frac{T'}{T}.$$

Applying this formula in above case  $V' = 44.5 \times \frac{760}{690} \times \frac{299}{273}$ .

**Exercise.** Find the volume of oxygen collected at 20° C. and 1000 mm. pressure obtained on heating 24.5 grams of potassium chlorate.

5.45 litres. **Answer.**

Hydrogen and oxygen unite to form two oxides of which the more important is HYDROGEN OXIDE, WATER, H<sub>2</sub>O.

**Preparation.** If one wished to prepare a large quantity of pure water it could be done by distilling some form of natural water, e.g. rain, river, spring, or sea water. Distil over about 20 c.c. of tap water from a small flask, using the apparatus figured and described on p. 13. Carry out the following experiments:—

(1) Evaporate about 3 c.c. of the distillate to dryness on a watch-glass placed on a water-bath. [Note. A water-bath is an



arrangement for heating by steam at ordinary pressure and generally consists of a copper vessel. In this case a beaker containing water will do. Put a folded piece of paper between the watch-glass and the beaker to allow for escape of steam, and then boil the water in the beaker.] Note that there is practically no residue. The apparatus is represented in Fig. 6.

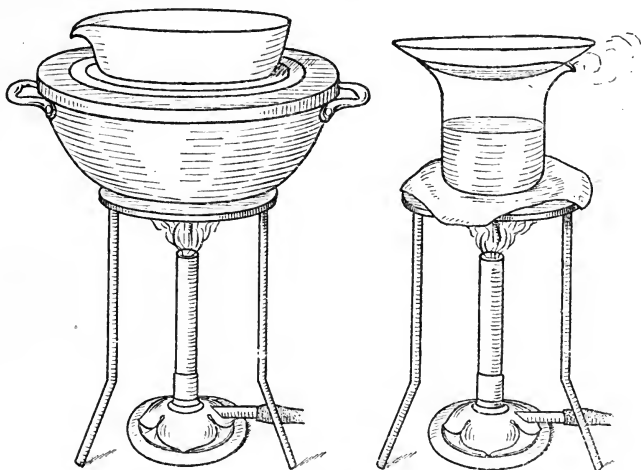


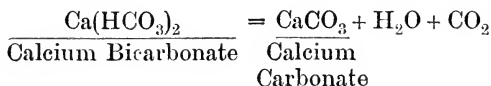
FIG. 6. COPPER WATER-BATH AND BEAKER USED AS WATER-BATH.

Now evaporate about the same volume of tap water. A distinct residue will be obtained.

(2) Add a few drops of a solution of silver nitrate to a few c.c. of distilled water and tap water in different test tubes. No reaction is obtained with the distilled water, but a white opalescence or precipitate is obtained with tap water. Tap water always contains chlorides, hence the reaction (cf. p. 197).

**Note.** The above differences between distilled and tap water explain why distilled water is generally used in analytical work.

(3) If the tap water happens to be 'temporarily hard' it will usually give a precipitate on boiling down, say, 100 c.c. to about half its bulk, owing to the decomposition of the bicarbonates of calcium and magnesium which are the cause of the temporary hardness.



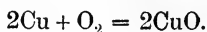
## 26 SIMPLE PREPARATIONS OF NON-METALLIC

(4) All tap waters contain dissolved air, as can be shown by boiling a sample in a round-bottomed flask of say 500 c.c. capacity filled with water, and connected by means of a rubber stopper with a delivery tube filled with water, the end of which is brought under a collecting tube in a trough of water. On boiling the water in the round flask the dissolved air is driven over into the collecting tube.

---

NITROGEN. SYMBOL N. Atomic weight 14. Density 14.

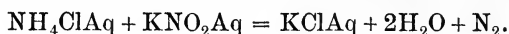
Nitrogen can be readily prepared from air in large quantity by passage over heated metallic copper, which withdraws oxygen and leaves the nitrogen.



Such nitrogen is impure, containing argon and other substances.

**Preparation.** A good method of preparing pure nitrogen in quantity would be to warm a solution containing sodium or potassium nitrite and ammonium chloride.

Nitrogen is evolved according to the equation



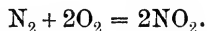
**Method of procedure.** Dissolve 5 grams of sodium nitrite and 10 grams of ammonium chloride in 50 c.c. of water and warm gently in a small flask fitted with a delivery tube passing under water. Fill several jars or test-tubes with the gas, and note the following properties:—

(1) The gas is odourless, colourless, tasteless, nearly insoluble in water.

(2) A glowing splint is extinguished, and the gas does not burn. Positive tests are more satisfactory than negative tests. They are hardly suited for a beginner, but are worth summarizing:—

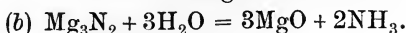
(a) Determination of density by weighing—14.

(b) Pass electric sparks through a mixture of oxygen and the gas over mercury. Brown fumes of nitrogen peroxide are obtained.



(c) Heat a small quantity of magnesium powder in the gas. Magnesium nitride is formed as a yellowish solid, which at once reacts on addition of a few drops of water to give ammonia, which can be recognized by its odour.

Equations :



### THE ATMOSPHERE. Density 14.43.

The atmosphere is a mechanical mixture of gases. There is usually approximately 21 per cent. of oxygen, 78 per cent. of nitrogen and 1 per cent. of argon and allies present, measured by volume. Carbon dioxide is present to the extent of about 0.03 per cent. by volume, water vapour in variable quantity, and traces of ozone ( $\text{O}_3$ ), ammonia ( $\text{NH}_3$ ), nitrogen peroxide ( $\text{NO}_2$ ). &c., may be present.

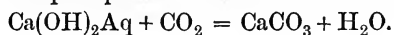
One can prove the presence of these gases in the following way:—

(1) Oxygen. On burning carbon, sulphur, magnesium, calcium, &c., identical products are obtained with those produced on burning in oxygen. The only difference apparent in the two sets of processes is that in the latter case the combustion is much more brilliant.

(2) Nitrogen. The nitrogen can be tested for by negative tests after removing the oxygen, or by passing electric sparks through a few c.c. of air over mercury. Brown fumes of nitrogen peroxide ( $\text{NO}_2$ ) are formed.

[(3) Argon and allied gases can best be proved to be present by removing the other constituents, and then investigating the spectra.]

(4) Carbon dioxide can be detected by drawing a considerable volume of air through lime-water, or by exposing a few cubic centimetres of lime-water on a watch-glass for some time. In either case a white precipitate of calcium carbonate is formed.



**Note.** There is far more carbon dioxide—over 100 times as much—in **respired air** than in atmospheric air, as can easily be proved by the following experiment. Fit up two test-tubes or small flasks closed by doubly-bored corks, through each of which pass two tubes in such a way that on connecting by a T-piece air can be drawn into the lungs through lime-water in one vessel and exhaled through lime-water in the other. In Fig. 7 the arrangement of the tubes is indicated.

In the solution through which the air passes into the lungs no precipitate is formed, but a copious precipitate is thrown down in the vessel through which the respired air passes.

(5) Water vapour can be tested for by exposing phosphorus pentoxide or calcium chloride for some time to air. Solutions are ultimately formed.

(6) Ozone could be tested for by means of starch iodide paper (i.e. paper which has been moistened with potassium iodide and

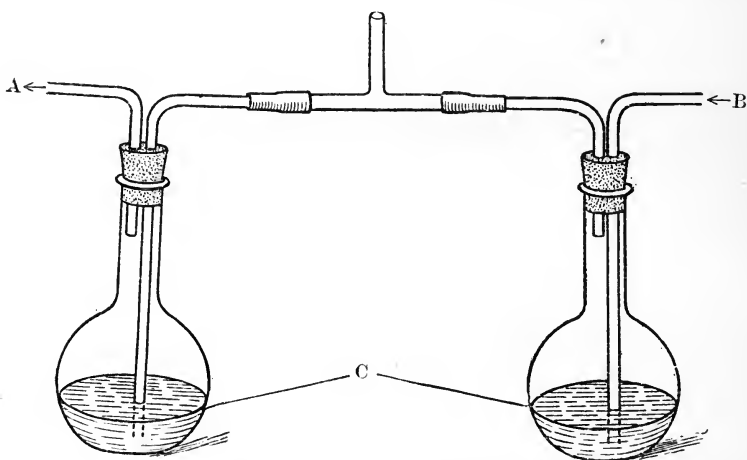
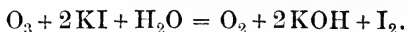


FIG. 7. APPARATUS FOR PROVING THAT RESPIRED AIR CONTAINS FAR MORE CARBON DIOXIDE THAN ORDINARY AIR. A, Respired Air forced out; B, Ordinary Air drawn in; C, Lime-water.

starch, and then dried). Such papers turn blue because of liberation of iodine and formation of starch iodide (see p. 36).



Nitrogen peroxide would also set free iodine.

Nitrogen forms several compounds with hydrogen. The most important is ammonia.

AMMONIA,  $\text{NH}_3$ . Molecular weight 17. Density 8.5.

**Preparation.** Heat a mixture of slaked lime and ammonium chloride in a small flask of hard glass, and pass the gas evolved first over lumps of quicklime,  $\text{CaO}$ , or sticks of caustic soda or potash to dry it, and then up into a small flask or large test-tube as represented in Fig. 8. Note the following properties:—

(1) The pungent characteristic odour. Do not attempt to smell the pure gas, but by motion of the hand cause convection currents which will bring a small quantity of the gas to the nostrils.

(2) Note the alkaline reaction by putting a piece of moist red litmus paper in the stream of gas. It will be turned blue immediately.

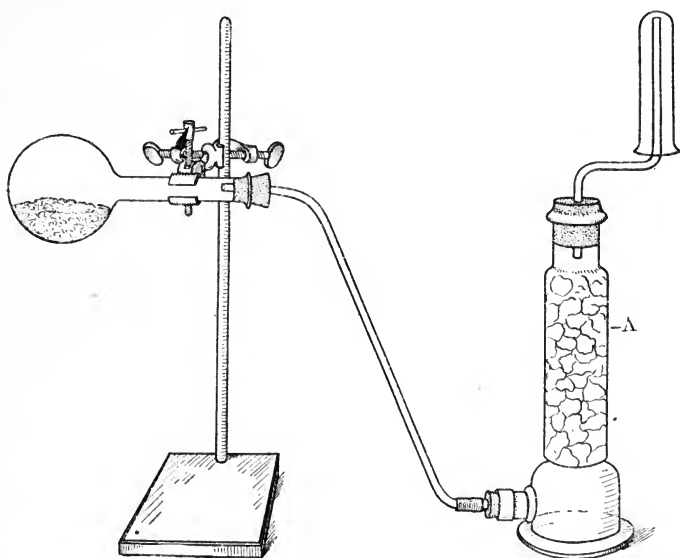
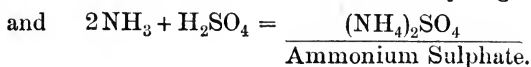
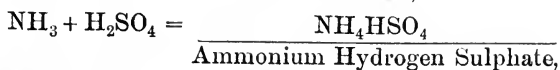
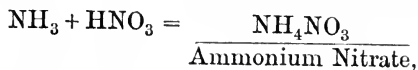
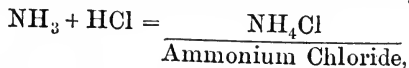


FIG. 8. PREPARATION OF AMMONIA. Collection by Upward Displacement (i.e. downward displacement of air). Δ, Drying Tower, containing lumps of Quicklime or Caustic Soda.

(3) Note the formation of white fumes on bringing a drop of any strong volatile acid, e.g.  $\text{HCl}$  or  $\text{HNO}_3$ , into the flask containing the gas. The white fumes are due to the formation of ammonium salts, since ammonia reacts directly with acids, e.g.



[**Note.** Concentrated sulphuric acid is often useful for drying other gases, e.g. hydrogen, oxygen, chlorine, &c., but is worse than useless for ammonia, as the above equations indicate. Ammonia must be dried by a basic substance such as quicklime or caustic potash, KOH.]

(4) Prove that the gas is extremely soluble in water by filling a small stout test-tube by upward displacement. Cover the end of the tube tightly by a small square of cardboard, put under water, and slip the card aside. The water will nearly fill the tube. The water would quite fill the tube if the ammonia were absolutely pure. The coefficient of solubility is 1140 at 0° C.

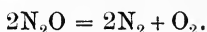
### OXIDES OF NITROGEN.

These are six in number and have the respective formulae  $N_2O$ ,  $NO$ ,  $N_2O_3$ ,  $NO_2$ , and  $N_2O_4$ ,  $N_2O_5$ . The oxides of nitrogen form an excellent example of the Law of Multiple Proportions.

**I. Nitrous Oxide ( $N_2O$ ).** Molecular weight 44. Density 22.

Prepare a small quantity of nitrous oxide by cautiously heating a few grams of ammonium nitrate in a small round-bottomed flask carrying a cork and delivery tube (cf. Fig. 5). Collect the gas by downward displacement or over warm water as the gas is somewhat soluble in cold water (coeff. 1.3 at 0° C.). The tubes may be closed by well-pressed corks. The sweetish odour and the anæsthetic properties can hardly be used as tests, but the following reactions are noteworthy:—

(1) Note that the gas rekindles a glowing splint in a similar manner to oxygen. The heat splits up the gas into nitrogen and oxygen, the latter gas reacting with the hot carbon.



(2) Half fill a test-tube with the gas over water and then pass up into the tube a few c.c. of nitric oxide during preparation of that substance. No reaction takes place. Oxygen at once reacts with nitric oxide to give a deep brown gas, nitrogen peroxide ( $NO_2$ ).

**II. Nitric Oxide,  $NO$ .** Molecular weight 28. Density 14.

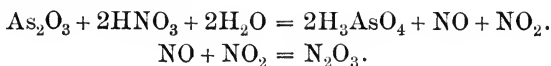
Place in a flask provided with a thistle funnel and delivery tube a few grams of copper turnings and then about 50 c.c. of dilute nitric acid. Warm gently. A brown gas seems to be evolved at first, but after a time the gas in the flask becomes colourless.

(a) Fill a tube with the gas over water, and then open the tube in air. Deep brown fumes are produced owing to reaction with the oxygen of the air.  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ . The brown fumes have a pungent characteristic odour, reminding one of nitric acid.

(b) Pass the gas through a solution of ferrous sulphate made by shaking a few crystals of that substance with water. The solution changes to a deep brown colour, owing to the formation of an addition compound  $\text{NO} \cdot 2\text{FeSO}_4$ .

III. Nitrogen Trioxide,  $\text{N}_2\text{O}_3$  (Nitrous Anhydride), is the anhydride of the unstable acid  $\text{HNO}_2$ .

This substance is unsuitable for laboratory preparation. Put a very small quantity of arsenious oxide in a test-tube, add a few drops of conc. nitric acid, and warm cautiously. A brown gas comes off which is a mixture of nitric oxide and nitrogen peroxide, and if condensed in a freezing mixture would give nitrogen trioxide as a blue liquid.



IV. Nitrogen Peroxide ( $\text{NO}_2$ ); and V. Nitrogen Tetroxide ( $\text{N}_2\text{O}_4$ ).

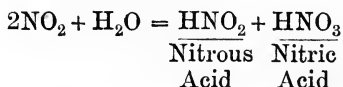
(1) Heat a few crystals of lead nitrate in a test-tube until the brown gas evolved fills the tube. Equation  $2\text{Pb}(\text{NO}_3)_2 = 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$ . Cautiously heat the tube along its length and note that the colour deepens. Loosely cork the tube and then put it into a Nessler glass (or into a wide test-tube) nearly filled with pounded ice and conc. hydrochloric acid. After allowing to stand for a few minutes note that the colour almost disappears. The reddish gas has condensed to form a modification called nitrogen tetroxide, which is colourless. Remove the tube from the freezing mixture, wipe dry, and heat: the colour reappears, the reaction being *reversible* as indicated by writing the equation  $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ .

The relationship between  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  is known as *polymerism*, the two gases being termed *polymeric modifications*.

DEFINITION. Polymerism is a term applied to the existence of two or more bodies with the same elements in the molecule, and the same relationship between the relative numbers of atoms of these elements, but the molecular weight of the one is a multiple of that of the other, and one can be readily transformed

into the other. A great many polymers are met with in Organic Chemistry.

(2) Test the solubility of the gas by filling a tube by downward displacement. Put the mouth of the tube under water and shake. The water rises and the brown colour disappears. Nitrogen peroxide reacts with water to give a mixture of nitrous and nitric acids.



#### VI. Nitrogen Pentoxide, $\text{N}_2\text{O}_5$ (Nitric Anhydride).

This body is an unstable white solid which is unsuitable for laboratory preparation, but can be obtained by warming gently nearly pure nitric acid and phosphorus pentoxide in a retort.

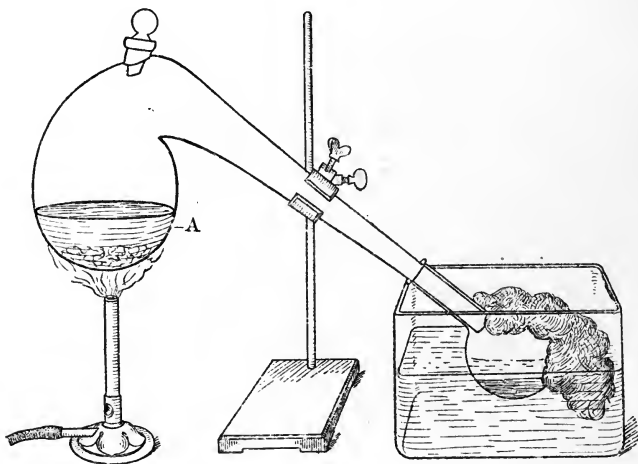
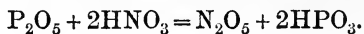


FIG. 9. PREPARATION OF NITRIC ACID. A, Retort.

NITRIC ACID,  $\text{HNO}_3$ . Liquid. B. pt.  $86^\circ\text{C}$ .

Prepare about 5 to 10 c.c. of nearly pure nitric acid by distilling slowly in a retort of 8–10 oz. capacity a mixture of 15–20 grams of potassium or sodium nitrate and excess of conc. sulphuric acid—say 20–30 c.c. Cool the small flask used in the receiver by placing in a basin of water and putting a moist cloth over the top as indicated in Fig. 9.



The yellowish liquid collecting in the receiver is coloured by nitrogen peroxide produced by decomposition of nitric acid.

Equations: (a)  $\text{KNO}_3 + \text{H}_2\text{SO}_4 = \text{KHSO}_4 + \text{HNO}_3$ .

(b)  $4\text{HNO}_3 = 2\text{H}_2\text{O} + 4\text{NO}_2 + \text{O}_2$ .

[Caution. The strong acid collected is extremely corrosive. It stains the skin yellow and raises blisters.]

Pure nitric acid is a colourless liquid, sp. gr. 1.5. The concentrated acid used in the laboratory is an aqueous solution containing about 70 per cent. of acid, sp. gr. 1.42.

Nitric acid is a powerful oxidizing agent. Carry out a selection of the following experiments illustrating this fact.

#### A. Experiments with the non-metals. C, S, P, I.

(1) Warm a few grams of sawdust on a firebrick placed over a Bunsen burner until it begins to char. Then pour a few drops of the acid prepared in above experiment upon it. The sawdust burns and brown fumes of nitrogen peroxide are produced.



(2) Boil up in a test-tube a small quantity of sulphur with the concentrated acid. The sulphur will be oxidized to sulphur trioxide (p. 42), which will form sulphuric acid with the water present. Test for sulphuric acid by adding barium chloride (p. 196), when a white precipitate of barium sulphate will come down.

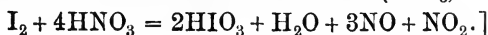
Equations:  $\text{S} + 2\text{HNO}_3 = \text{H}_2\text{SO}_4 + 2\text{NO}$ .

$\text{S} + 4\text{HNO}_3 = \text{H}_2\text{SO}_4 + \text{H}_2\text{O} + 3\text{NO}_2 + \text{NO}$ .

[(3) Phosphorus can be oxidized similarly to phosphoric acid, which may be tested for by addition of ammonium molybdate and warming (p. 201).



[(4) Iodine would be oxidized to iodic acid ( $\text{HIO}_3$ ).



#### B. Reactions with metalloids and metals. Sb, As, Sn, Cu.

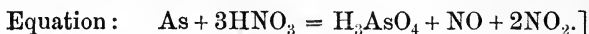
Arsenic, antimony, and tin are merely oxidized, but most metals are oxidized and converted to salts.

(5) Warm a small quantity of powdered antimony with nitric acid. The antimony is oxidized to antimony pentoxide, which separates (hydrated) as a white powder.

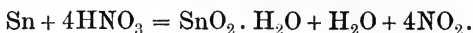
Equation:  $2\text{Sb} + 4\text{HNO}_3 = \text{Sb}_2\text{O}_5 \cdot \text{H}_2\text{O} + 3\text{NO} + \text{NO}_2$   
 $2\text{HSbO}_3$  (Metantimonic Acid).

## 34 SIMPLE PREPARATIONS OF NON-METALLIC

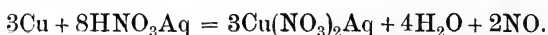
[(6) Warm a small quantity of powdered arsenic with the acid. It goes into solution as arsenic acid.



(7) Warm a few small pieces of granulated tin with concentrated nitric acid. Dense brown fumes are evolved and the tin is oxidized to stannic oxide,  $\text{SnO}_2$ .



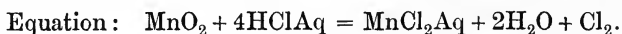
(8) Copper is at once dissolved. Ag, Bi, Hg, and Pb would behave similarly.



### THE HALOGEN ELEMENTS. (F), Cl, Br, I.

**Chlorine.** Symbol Cl. Atomic weight 35.5. Density 3.5.

**Preparation I.** Prepare chlorine by warming in a flask a mixture of manganese dioxide (preferably granular) and concentrated hydrochloric acid.



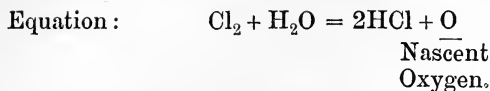
The flask is closed by a cork carrying a thistle funnel and a tube for collection by downward displacement as indicated in Fig. 10. Fill a few test-tubes or small jars and also prepare a solution by saturating about 20 c.c. of water with the gas in a small flask. The preparation should preferably be carried out in a fume cupboard. Note the greenish-yellow colour and pungent odour, but (**Caution**) great care should be taken to avoid inhaling even a small quantity of the pure gas. Carry out the following experiments:—

(a) Shake into a vessel containing gas a small quantity of finely powdered antimony. A vigorous reaction takes place with evolution of light and heat, the antimony forming antimonious chloride ( $\text{SbCl}_3$ , solid); and the pentachloride ( $\text{SbCl}_5$ , liquid).

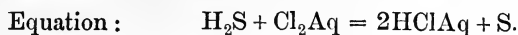


(b) Yellow phosphorus will react directly with chlorine to form similar compounds, viz.  $\text{PCl}_3$  (liquid) and  $\text{PCl}_5$  (solid).

(c) Note the 'bleaching action'. Put a piece of moist blue litmus paper into the gas. It first turns red and then white. The bleaching effect is due to nascent oxygen set free by interaction of the chlorine and water in presence of an oxidizable body.

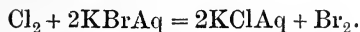


(d) Pass sulphuretted hydrogen through a solution of chlorine water. A precipitate of sulphur is thrown down.



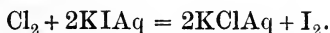
(e) Add about one c.c. of chlorine water to a few c.c. of potassium bromide solution. Bromine is set free and the liquid turns brown.

Equation:



Add about one c.c. of carbon disulphide ( $\text{CS}_2$ ) or chloroform ( $\text{CHCl}_3$ ) and shake. The bromine being much more soluble in  $\text{CS}_2$  or  $\text{CHCl}_3$  than in water dissolves to give a reddish orange solution in the  $\text{CS}_2$  or  $\text{CHCl}_3$ , which settles at the bottom of the test-tube.

(f) Carry out a similar experiment to (e) with potassium iodide solution. Iodine is set free, giving a brown solution, but on shaking with  $\text{CS}_2$  or  $\text{CHCl}_3$  a violet solution will settle.



**Preparation II.** Chlorine can be readily prepared by warming a mixture of any chloride, e.g.  $\text{NaCl}$  or  $\text{KCl}$  with powdered manganese dioxide and concentrated or slightly diluted sulphuric acid.

**Bromine.** At. wt. 80. Liquid. B. pt.  $63^\circ\text{C}$ . Sp. gr. 3.1.

**Preparation.** Mix intimately about 2 grams of powdered potassium bromide and an equal weight of manganese dioxide. Place in a small retort of about 8 oz. capacity, moisten with water, and then add about 10 c.c. of concentrated sulphuric

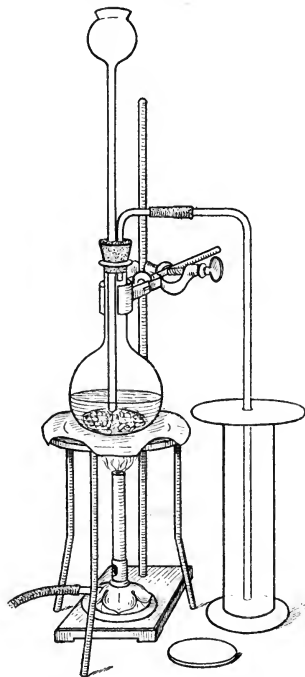
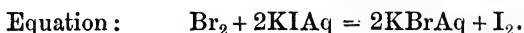


FIG. 10. PREPARATION OF CHLORINE. Collection by Downward Displacement (or upward displacement of air).

acid and warm gently. Use a small flask as receiver, and cool as in the case of nitric acid (see Fig. 9). Bromine comes off as a deep brown vapour which condenses in the receiver, forming a dark brown liquid. Add water to the receiver and shake. A brown solution called bromine water is obtained. Experiments:—

(a) Add about one c.c. of bromine water to a few c.c. of a solution of potassium iodide. Iodine is liberated as indicated by the violet colour on shaking up with  $\text{CS}_2$  or  $\text{CHCl}_3$ .



(b) Pass sulphuretted hydrogen through bromine water. The solution becomes colourless, and a precipitate of sulphur is formed.



**Iodine.** At. wt. 127. Grey solid m. pt.  $114^\circ\text{C}$ . B. pt.  $184^\circ\text{C}$ .

Prepare a small quantity of iodine by mixing a couple of grams of powdered potassium iodide with about 4 grams of manganese dioxide, moistening with water in a small porcelain dish, then adding a few c.c. of concentrated sulphuric acid, covering the dish with another, and warming gently. A sublimate of iodine is obtained as a grey solid on the upper dish.

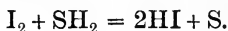
NOTE.—(a) Colour of the vapour on heating—a beautiful violet.

(b) The very slight solubility in water.

(c) The ready solubility in potassium iodide solution.

(d) The deep blue colour obtained by adding one drop of the solution in potassium iodide to a small quantity of freshly prepared starch solution. Note.—To prepare this solution take a small granule of starch about the size of a pea, crush to a powder between the fingers, add a few c.c. of water, and boil for about a minute.

(e) Pass sulphuretted hydrogen through the solution of iodine in potassium iodide. A precipitate of sulphur is formed, and the solution becomes colourless.



**THE HALOGEN HYDRACIDS.** (HF), HCl, HBr, HI.

All acids must contain hydrogen, but most contain oxygen as well; in fact, the replaceable hydrogen is generally hydrogen of

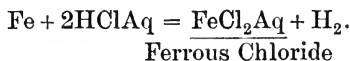
**hydroxyl**, the name given to the group  $\text{—O—H}$ . The above halogen acids are therefore exceptional.

**Hydrochloric Acid, HCl.** Mol. wt. 36.5. Density 18.25. Put a few grams of rock-salt or common salt into a small flask, which can be closed by a cork carrying a thistle funnel and tube for collection by downward displacement (see Fig. 9). Add gradually strong sulphuric acid. Fill a test-tube with the gas. Note that it is colourless but fumes in air because of condensation of the moisture present. Note also the pungent odour and strongly acid reaction. Prove its great solubility by covering the mouth of the tube with a piece of cardboard, inverting, and immersing in water.

By a selection of experiments the student should convince himself of the truth of the following statements:—

(1) Hydrochloric acid does not react with Au, Pt, Hg, or Cu, and very slowly with silver, lead, arsenic, antimony, or bismuth. It should therefore not be used as a solvent for these metals.

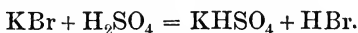
(2) It reacts with other metals liberating hydrogen, but in cases where two salts of one metal can be obtained (e. g. iron) the ‘-ous’ compound (that is, the compound with the smaller quantity of chlorine per atom of metal) is obtained, e. g.



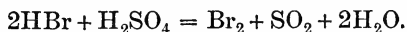
If potassium ferricyanide is added to the solution obtained by dissolving iron in hydrochloric acid, a deep blue precipitate is obtained, proving the presence of a ferrous salt (p. 116).

**Hydrobromic Acid, HBr.** Mol. wt. 81. Density 40.5. Carry out the following experiment:—

Try a method analogous to that used for the preparation of hydrochloric acid, namely addition of sulphuric acid to potassium bromide (KBr). On warming about a gram of potassium bromide with concentrated sulphuric acid in a test-tube a gas is evolved which fumes in air like hydrochloric acid, but the tube soon fills with brown fumes of bromine and  $\text{SO}_2$  is also present. Two reactions take place. (a) HBr is liberated.



(b) The hydrobromic acid reacts with the concentrated sulphuric acid.



The method is therefore not available for preparation of hydrobromic acid.

## 38 SIMPLE PREPARATIONS OF NON-METALLIC

Either glacial phosphoric acid should be used or bromine be added to red phosphorus covered by a layer of water. (See Theoretical Book.)

**Hydriodic Acid, HI.** Mol. wt. 128. Density 64. Hydriodic acid is similar in preparation and properties to hydrobromic acid.

Add sulphuric acid to about one gram of potassium iodide in a test-tube. Hydriodic acid, sulphur dioxide, and iodine are set free. This method is therefore unsuitable for the preparation of hydriodic acid.

Equations: (a)  $KI + H_2SO_4 = KHSO_4 + HI$ .

(b)  $2HI + H_2SO_4 = 2H_2O + SO_2 + I_2$ .

**CARBON.** Atomic weight 12.

**Preparation.** Heat cautiously about a gram of sugar or starch in a small closed crucible. The mass chars, froths up, and finally a residue of nearly pure carbon is left.

### THE OXIDES OF CARBON.

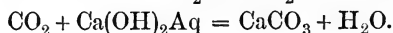
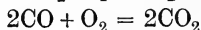
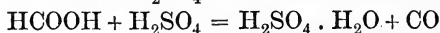
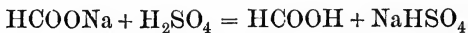
I. Carbon Monoxide,\* CO.

II. Carbon Dioxide or Carbonic Anhydride, CO<sub>2</sub>.

**Carbon Monoxide, CO.** Mol. wt. 28. Density 14.

(1) Fill a test-tube with carbon monoxide by warming gently about a gram of sodium formate with one c.c. of concentrated sulphuric acid in a test-tube carrying a delivery tube for collection over water. Add about 2 c.c. of lime-water, and shake. No reaction occurs. Set fire to the gas. It burns with a blue flame, forming carbon dioxide. On shaking the lime-water is rendered turbid.

Equations:

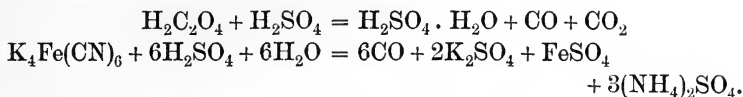


**Caution.** Care should be taken not to inhale much of the gas, as it is very poisonous, combining with the haemoglobin of the blood to form carboxy-haemoglobin.

\* The term carbonic oxide, formerly applied to this compound, should not be used.

(2) The gas could also be obtained from oxalic acid or potassium ferrocyanide by warming with concentrated sulphuric acid. (See Textbook.)

Equations:



Although water appears in the last equation it must not be added to the reaction mixture, as it is present in sufficient quantity in the sulphuric acid and as water of crystallization of the ferrocyanide. Dilute sulphuric acid would give hydrocyanic acid.

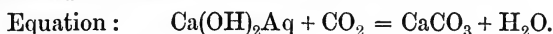
**Test.** The combustion with blue flame to form carbon dioxide is characteristic.  $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ .

A more delicate test (e. g. for small quantities in air) could be carried out by shaking a considerable volume with a few c.c. of very dilute blood solution and then examining spectroscopically. A characteristic double-banded absorption spectrum is obtained.

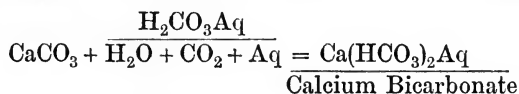
**Carbon Dioxide,  $\text{CO}_2$ .** Mol. wt. 44. Density 22.

Prepare carbon dioxide by adding dilute hydrochloric acid to a few small pieces of marble in a flask provided with a thistle funnel and delivery tube (see Fig. 4). Collect over water or by downward displacement.

Note that the gas neither burns nor supports combustion, but gives a precipitate on shaking with lime-water.



With excess of carbon dioxide the precipitate which first forms redissolves because of the formation of a soluble bicarbonate.



**Note.** This last reaction is important in nature. Limestone rocks are dissolved in this way by the carbonic acid dissolved in rain water.

**Sulphuretted Hydrogen.** Mol. wt. 34. Density 17.

Prepare sulphuretted hydrogen by treating ferrous sulphide with dilute sulphuric acid in a flask fitted with thistle funnel and delivery tube (see Fig. 4). Fill a few jars or test-tubes by downward displacement, as the gas is soluble in water. Then

## 40 SIMPLE PREPARATIONS OF NON-METALLIC

pass the gas into about 20 c.c. of water in a small flask, shaking from time to time until the liquid is saturated.

NOTE. (1) Disagreeable odour.

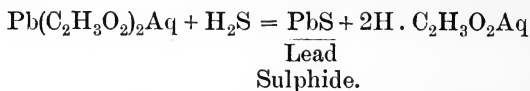
(2) The gas burns with a blue flame, forming water and sulphur dioxide, the latter gas being recognized by its odour of burning sulphur. Equation:  $2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{H}_2\text{O} + 2\text{SO}_2$ .

(3) The acid character. Moist blue litmus paper is slowly turned red. Sulphuretted hydrogen is a weak acid, both hydrogen atoms being replaceable by metal.

(4) Paper moistened with a soluble salt of Pb, Ag, Hg, Cu or Bi is turned nearly black on immersion in the gas.

Test. The usual test for the gas besides the characteristic odour is the reaction with paper moistened with lead acetate.

Equation:

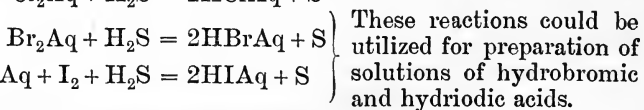
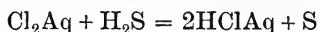
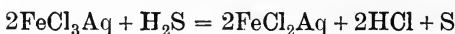
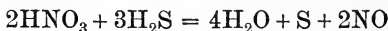


(5) The gas is a strong reducing agent and reacts with many oxidizing agents, e. g. nitric acid, chlorine water, bromine water, iodine in potassium iodide solution, arsenates, ferric salts, concentrated sulphuric acid, potassium permanganate, and potassium chromate and dichromate. As sulphuretted hydrogen is an important reagent in detection of metals, the reactions are notable, since the presence of any of the above bodies in solution may interfere with the ordinary reactions. The reactions with nitric acid and ferric salts are especially important.

Add a few c.c. of the sulphuretted hydrogen solution to a few c.c. of each of the following bodies:—

(a) Dilute nitric acid, (b) ferric chloride solution, (c) chlorine water (p. 35), (d) bromine water (p. 36), (e) solution of iodine in potassium iodide solution (cf. p. 36), (f) sulphurous acid solution. Note that in each case a precipitate of sulphur is thrown down.

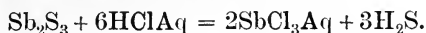
Equations:





**Preparation of pure sulphuretted hydrogen.**

The above method of preparation does not yield a pure product since ferrous sulphide is usually contaminated with iron. A pure sample could be obtained by warming antimonious sulphide ( $\text{Sb}_2\text{S}_3$ ) with concentrated hydrochloric acid.

**OXIDES OF SULPHUR,  $\text{SO}_2$ , ( $\text{SO}_3$ ).**

**I. Sulphur Dioxide** (Sulphurous Anhydride),  $\text{SO}_2$ . Mol. wt. 64. Density 32.

Prepare sulphur dioxide by warming copper turnings with concentrated sulphuric acid in a flask fitted with a thistle funnel and delivery tube (see Fig. 10). Fill a test-tube with the gas by downward displacement, and then prepare a solution by passing the gas into a few c.c. of water in a flask.

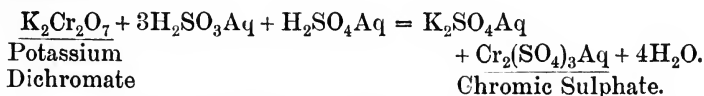
**Note.** (1) The characteristic odour of burning sulphur.

(2) The gas is non-combustible and does not support combustion.

(3) It is strongly acid in reaction.

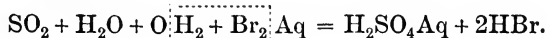
(4) The body is a strong reducing agent. It converts arsenates to arsenites, chromates and dichromates to chromic salts, and solution of cupric chloride to cuprous chloride. Put a piece of filter paper moistened with potassium dichromate into the gas. The paper turns green because of reduction of the dichromate to chromic salt.

Equation :



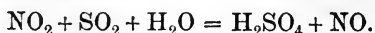
(5) Carry out tests to prove that it is at once oxidized by certain bodies, e. g.  $\text{NO}_2$ ,  $\text{Cl}_2\text{Aq}$ ,  $\text{Br}_2\text{Aq}$ , which transform the dioxide into trioxide, and the latter, since water is present, immediately forms sulphuric acid.

(a) Add bromine water to some of the solution. Note that the brown colour at once disappears and that the liquid contains sulphuric acid, as can readily be proved by adding barium chloride solution, when a white precipitate of barium sulphate is formed insoluble in acids.



## 42 SIMPLE PREPARATIONS OF NON-METALLIC

(b) Pass  $\text{NO}_2$  into a solution of sulphur dioxide, and then test the liquid for sulphuric acid.



This is the chief reaction in the preparation of sulphuric acid on the large scale.

### II. Sulphur Trioxide (Sulphuric Anhydride), $\text{SO}_3$ .

This substance is not suited for preparation by one beginning the subject. It is a white fuming solid which reacts vigorously with water to form sulphuric acid ( $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ ), and is obtained by passing a dry mixture of sulphur dioxide and oxygen over warmed platinized asbestos.  $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ .

## SULPHURIC ACID, $\text{H}_2\text{SO}_4$ .

Two methods of preparation have been indicated above. The pure acid is an oily liquid, sp. gr. 1.85, which reacts vigorously with water. **Caution.**—It must never be added to a hot solution.

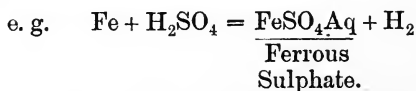
Although rarely used as a solvent the following general properties of the acid are worth remembering, and the student should be able to devise experiments to verify the statements.

The dilute and concentrated acid respectively behave quite differently with metals, the dilute acting like hydrochloric acid (p. 37) and the concentrated acid like nitric acid (p. 33).

### A. Dilute Sulphuric Acid.

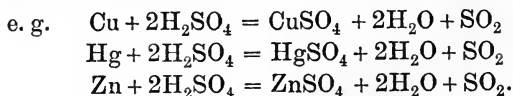
The dilute acid does not act upon Au, Pt, Ag, Cu, Hg, and acts with difficulty upon Pb, As, Sb, Bi.

When it does act hydrogen is evolved, and if the metal forms two salts the -ous compound is obtained.



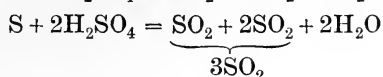
### B. Concentrated Sulphuric Acid.

(1) The concentrated acid does not act upon Au and Pt, but reacts with most other metals with evolution of sulphur dioxide.



In this last case sulphuretted hydrogen is also formed.

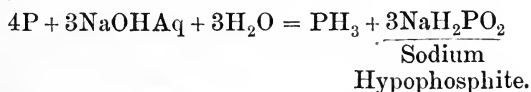
(2) Hot concentrated sulphuric acid is also a powerful oxidizing agent, e. g. it gives up oxygen to carbon and sulphur, which form dioxides.



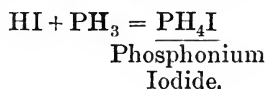
## COMPOUNDS OF PHOSPHORUS.

### Phosphoretted Hydrogen, $\text{PH}_3$ .

This gas is unsuitable for general laboratory preparation. It can be obtained by heating yellow phosphorus with caustic soda or potash.

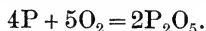


It is nearly insoluble in water, is poisonous, and has the odour of decaying fish. The compound is the chemical analogue of ammonia, and forms similar salts with acids, e. g.

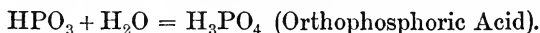
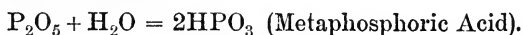


### Phosphorus Pentoxide, $\text{P}_2\text{O}_5$ .

This substance is a white, very hygroscopic solid obtained by burning phosphorus in excess of air or oxygen.

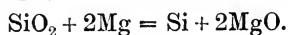
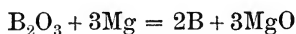


It dissolves in cold water, forming metaphosphoric acid, and on boiling the solution orthophosphoric acid is obtained, as could be proved by tests (p. 201).



### Boron, B. At. wt. 11. Silicon, Si. At. wt. 28.

These two elements can be prepared by heating excess of the oxides with magnesium powder in a closed crucible to a high temperature.



## 44 NON-METALLIC ELEMENTS AND COMPOUNDS

After removal of the magnesium oxide by dilute hydrochloric acid, and filtering, the elements are obtained as nearly black powders, which glow in air when strongly heated, forming the oxides ( $B_2O_3$  and  $SiO_2$ ).

These oxides are anhydrides of boracic ( $H_3BO_3$ ) and silicic acids ( $H_2SiO_3$  and  $H_4SiO_4$ ) respectively.

## MEMORANDA

## MEMORANDA

## **PART II**

### **PREPARATION OF TYPICAL COMPOUNDS OF THE METALS**

- A. Preparation of Metallic Salts**
- B. Preparation of Metallic Oxides and Hydroxides**





## PART II

### PREPARATION OF TYPICAL COMPOUNDS OF THE METALS

**A. Preparation of Metallic Salts.**

**B. Preparation of Metallic Oxides and Hydroxides.**

### PREPARATION OF TYPICAL COMPOUNDS OF THE METALS

So far only **non-metals** and their compounds have been considered. Taking the usual scheme followed in theoretical work one would next come to the **metals** and their important compounds. As regards the metals themselves a few preparations in the dry way (e. g. Pb, Ag, Cu, Bi, Sb) and in the wet way (e. g. Hg, As, Sb) are of importance for purposes of identification, and are described under the tests for the metals.

One might merely indicate here that the experiments carried out already, especially those in connexion with oxygen, have indicated the **main chemical distinctions between Non-metals and Metals**, namely, that **Non-metals** (a) do not replace the hydrogen of acids to form salts, and (b) form oxides which are usually acid anhydrides, whereas **Metals** (a) do replace the hydrogen of acids to form salts, and (b) form as a rule basic oxides and hydroxides.

Various physical distinctions, such as the metallic lustre, and the greater malleability, ductility, tenacity, and conducting power for heat and electricity of the metals, as well as the general comparatively low specific gravity of the non-metals, will be found discussed in theoretical books.

#### A. PREPARATION OF METALLIC SALTS

**DEFINITION.** Salts are compounds derived from acids by replacing part or all the replaceable hydrogen by metals (or metallic radicles, e. g. SbO antimonyl).

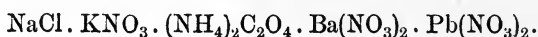
There are four important types of salt met with in elementary chemistry, viz. :—

- (1) Normal salts
- (2) Acid       ,,
- (3) Basic       ,,
- (4) Double     ,,

(1) **DEFINITION.** Normal Salts are compounds derived from acids by replacing all the replaceable hydrogen by metal.

The reaction of these salts towards indicators is frequently neutral, but may be alkaline or acid ;

e. g. (a) Normal salts of neutral reaction :—



(b) Normal salts with alkaline reaction :— $\text{K}_2\text{CO}_3 . \text{Na}_2\text{CO}_3 . \text{KCN}$ .

(c) Normal salts with acid reaction :— $\text{CuSO}_4 : \text{ZnSO}_4 : \text{Al}_2(\text{SO}_4)_3$ .

(2) **DEFINITION.** Acid Salts are compounds derived from acids by replacing part of the replaceable hydrogen by metals. The reaction of acid salts towards indicators is generally acid, but may be neutral or alkaline.

e. g.  $\text{KHSO}_4 : \text{NaHSO}_4 : \text{NaH}_2\text{PO}_4$  and  $\text{KHC}_4\text{H}_4\text{O}_6$  are acid in reaction, and  $\text{Na}_2\text{HPO}_4$  (common sodium phosphate or disodium hydrogen phosphate) is nearly neutral—faintly alkaline.

(3) **DEFINITION.** Basic Salts are compounds in which the metal functions partly as oxide or hydroxide (i. e. functions partly as base) and is partly combined with an acid radicle or radicles ;

e. g.  $\text{Bi}(\text{OH})_2 . \text{NO}_3 : \text{BiOCl} : \text{SbOCl}$ .

Basic salts are frequently insoluble, so that their reaction to indicators is not readily determined, but a few are soluble and generally alkaline in reaction ;

e. g. basic lead acetate,  $\text{Pb}(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)$ .

**DEFINITION.** In Double Salts two salts are united together in some simple ratio of their molecular proportions, generally molecule to molecule ; e. g. common alum,  $\text{K}_2\text{SO}_4 . \text{Al}_2(\text{SO}_4)_3 . 24\text{H}_2\text{O}$ .

**NOTE.** The preparation of double salts is not quite suitable for an elementary course.

**Crystallization.** In preparing salts one generally tries to obtain crystals. Most salts can be obtained in crystalline form under suitable conditions, and the following factors influencing crystallization must be taken into consideration :—

(a) The purity of the compound. As a rule the purer a compound is, the more readily will it crystallize.

(b) The solvent. Most metallic crystalline salts are soluble in water, and insoluble in alcohol and other organic solvents. Water is the general solvent employed for inorganic salts, and also for metallic salts of organic acids. Many compounds of carbon (i. e. organic compounds) are insoluble in water, but readily soluble in alcohol, ether, and other organic solvents from which they can be crystallized.

(c) Variation of solubility with temperature. If the increase of solubility with rise of temperature be small, as a rule it will be difficult to obtain large crystals in a short time and vice versa.

(d) Time allowed for crystallization. Crystals grow by accretion round nuclei, which generally form spontaneously when a liquid saturated at a temperature above that of the room, is allowed to cool. In order that large crystals may be obtained, the liquid should be saturated at its boiling-point, and the rate of cooling should be slow.

(e) Rapid convection currents will prevent regular crystallization, and therefore the solution should after saturation be placed upon a bad conductor, such as a filter pad, and should be covered so as to hinder surface cooling.

### Methods of Preparation.

In selecting a method of preparation for any particular compound, the following general methods of obtaining salts should be kept in view.

#### I. Methods suitable for soluble salts.

(1) Action of Acid upon a Base (i. e. upon the metallic oxide or hydroxide).

(2) Action of Acid upon a Carbonate.

(3) Direct replacement of the hydrogen in an acid by the metal.

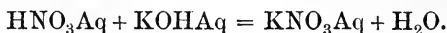
#### II. Method suitable for insoluble or sparingly soluble compounds.

(4) Precipitation.

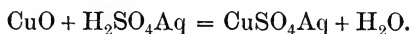
#### I. Methods suitable for soluble salts.

1. Action of an Acid upon a Base, i. e. action of acid upon the metallic oxide or hydroxide.

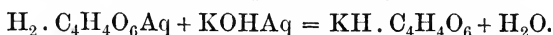
e. g. (a) Preparation of potassium nitrate (nitre) from nitric acid and potassium hydroxide.



(b) Preparation of crystallized copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) from copper oxide and dilute sulphuric acid ;



(c) Preparation of acid potassium tartrate (cream of tartar) from tartaric acid ( $\text{H}_2 \cdot \text{C}_4\text{H}_4\text{O}_6$ ) and potassium hydroxide ;

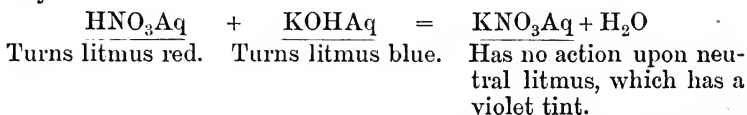


These three reactions are typical and require further consideration. The first and second represent the preparation of normal salts, and the third of an acid salt.

#### Preparation of Normal Salts :—

(a) Preparation of Potassium Nitrate from Nitric Acid and Potassium Hydroxide.

In this preparation the acid is said to be neutralized by the base, or conversely. This means that the acid reaction of the acid is destroyed by the addition of the proper proportion of base. If one adds more than the required quantity of base, the reaction mixture will have an alkaline reaction, and the salt will not crystallize so readily and will be impure. Many indicators could be used for testing neutrality, but litmus is generally the most convenient. As we have already seen, acids turn litmus red, and soluble bases turn litmus blue. A neutral salt has no action upon litmus. The conditions required in a successful experiment might be emphasized by writing the neutralization in the following way :—



The exact method of procedure is indicated below in describing the preparation of the body in detail (p. 57).

(b) Preparation of Copper Sulphate from Copper Oxide and dilute Sulphuric Acid.

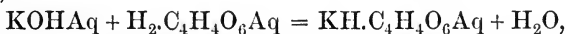
Copper sulphate is, like potassium nitrate, a normal salt, but it is acid in reaction. We cannot therefore boil up copper oxide (the base) with sulphuric acid until a neutral reaction is obtained. We must in this case merely make certain that a sufficiency of

base has been added by boiling dilute sulphuric acid with copper oxide until a small quantity of oxide remains unaltered after boiling for say ten minutes. The liquid is then filtered off and evaporated to crystallization.

NOTE. If an insufficiency of base is used when sulphuric acid is the solvent, it will in many cases be difficult to get crystals, especially if the salt contains water of crystallization. In this case, for example, if excess of sulphuric acid be used, a greenish white powder of nearly anhydrous copper sulphate will be obtained on evaporation instead of deep blue crystals of the composition  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

### (c) Preparation of Potassium Hydrogen Tartrate from Tartaric Acid and Potassium Hydroxide.

The preparation of potassium hydrogen tartrate is typical for acid salts. On inspection of the equation representing the reaction,



we should understand that in the formula for tartaric acid ( $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ ), which is a dibasic acid, the two hydrogen atoms taken to the left of the molecule are replaceable, and obviously only one of them is replaced in the salt ( $\text{KH}\text{C}_4\text{H}_4\text{O}_6$ ). The acid may be said, therefore, to be only half neutralized, and the product is strongly acid. We cannot proceed, therefore, as described above in experiment (a), but can, without weighing, use the proper quantity of acid by proceeding as follows. Take a certain volume of tartaric acid solution (say 50 c.c. of concentrated solution), and divide it into two equal parts. Take one half (25 c.c.), and neutralize with potassium hydroxide, using litmus as indicator, and then add to the neutral solution the other half (25 c.c.) of the acid solution, which will be exactly sufficient to form the acid salt required.

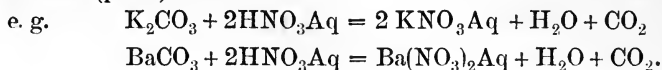
### 2. Action of the Acid upon the Carbonate of the Metal.

This is an excellent method for preparing many salts, e. g.  $\text{KNO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{Cl}$ , &c.

One generally puts a solution of the acid in a dish or beaker, and gradually adds carbonate of the metal.

Carbonic acid ( $\text{H}_2\text{CO}_3$ ) is set free and decomposes into water and carbon dioxide, the latter escaping as a gas with effervescence. This escape of gas affords a ready means of telling when we are just about to reach the end of the reaction. When about enough

has been added, boil to get rid of carbon dioxide, and test for neutrality with litmus paper as described below under Potassium Nitrate (p. 57).



**3. Direct Replacement of Hydrogen in an Acid by Metal,**  
e. g. preparation of ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

One boils up the acid with excess of metal present until hydrogen ceases to be evolved, and then filters and evaporates to crystallization. In using this method one should know what metals are attacked by the different acids. To a certain extent this has been already indicated, but the following summary might prove useful:—

**A. Metals insoluble in Hydrochloric Acid:** Au, Pt, Cu, Hg.

**Metals very slightly soluble in Hydrochloric Acid:** Ag, As, Sb, Bi, Pb.

This general method of preparation would therefore not be available for the chlorides of these nine metals.

**B. Metals insoluble in Nitric Acid:** Au, Pt.

NOTE. Antimony and tin are oxidized by nitric acid (see p. 33).

**C. In considering the solubility of metals in Sulphuric Acid** one must note that dilute and concentrated acid may have different effects (cf. p. 42). The dilute acid reacts like hydrochloric acid, and the concentrated acid like nitric acid.

**(a) Metals insoluble in dilute Sulphuric Acid:** Au, Pt, Cu, Hg, Ag.

**Metals slightly soluble in Sulphuric Acid:** As, Sb, Bi, Pb.

**(b) Metals insoluble in concentrated Sulphuric Acid:** Au, Pt.

Although concentrated sulphuric acid acts upon most metals it is not a convenient solvent. The reaction takes place on heating and sulphur dioxide is generally evolved. It is difficult to get rid of excess of acid. The preparation of a sulphate from the metal as starting-point, in the case of a metal unacted upon by dilute sulphuric acid but dissolved by the concentrated acid, is generally better carried out by making a solution of the nitrate, preparing from this solution the oxide, hydroxide, or carbonate, and then reacting with dilute sulphuric acid (Method (b)).

## II. Method of Preparation suitable for insoluble or sparingly soluble compounds.

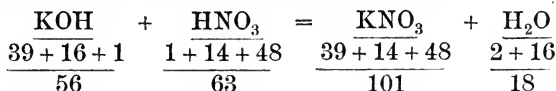
### 4. Precipitation.

A very large number of salts can be prepared by this method. It is obvious that before one can properly apply the method the solubility of the more important classes of salts must be known. The matter is more fully treated later on (p. 94 et seq.), but a brief summary of insoluble or sparingly soluble compounds may for convenience be given here:—

- (1) **Chlorides.**  $\text{PbCl}_2$ ,  $\text{HgCl}$ ,  $\text{AgCl}$ ,  $\text{SbOCl}$ ,  $\text{BiOCl}$ ,  $(\text{Cu}_2\text{Cl}_2)$ .
- (2) **Bromides.**  $\text{PbBr}_2$ ,  $\text{HgBr}$ ,  $\text{AgBr}$ .
- (3) **Iodides.**  $\text{PbI}_2$ ,  $\text{HgI}$ ,  $\text{HgI}_2$ ,  $\text{AgI}$ ,  $(\text{Cu}_2\text{I}_2)$ .
- (4) **Nitrates.** Only a few basic compounds, e. g.  $\text{Bi}(\text{OH})_2\text{NO}_3$ .
- (5) **Sulphates.**  $\text{CaSO}_4$ ,  $(\text{SrSO}_4)$ ,  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ .
- (6) **Carbonates.** All insoluble except those of Na, K, and  $\text{NH}_4$  and a few acid carbonates, e. g.  $\text{Ca}(\text{HCO}_3)_2$ .
- (7) **Phosphates.** All insoluble except those of Na, K,  $\text{NH}_4$  and a few acid phosphates, e. g.  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .
- (8) **Sulphides.** All insoluble except those of Na, K,  $\text{NH}_4$ . A few react with water, e. g.  $\text{Al}_2\text{S}_3$ ,  $\text{Cr}_2\text{S}_3$ ,  $\text{CaS}$ ,  $\text{BaS}$ ,  $\text{MgS}$ .

**General Note regarding quantities employed for Preparations.** We should aim at getting a moderate quantity (say 4–10 grams) of the product. Such quantities can be conveniently prepared in a small beaker (250 c.c.), or in a porcelain dish of 4–5 inches diameter, and can be spread out on a four-inch clock-glass or filter paper.

The quantities of material required can be calculated from the equation representing the reaction in any particular case, but as one rarely gets the whole of the substance unless in the case of a precipitation, one should assume that we will only obtain 50–80 per cent. of the theoretical yield, and should therefore roughly weigh out quantities, which should theoretically yield 10–12 grams of the substance required; e. g. the equation representing the preparation of potassium nitrate is:—



The equation shows that 56 grams of caustic potash would yield 101 grams of potassium nitrate when neutralized by nitric

acid; therefore 5.6 grams of caustic potash would yield 10.1 grams of potassium nitrate ( $\text{KNO}_3$ ). As nitre is fairly soluble in water 30–40 per cent. may remain in solution, and therefore in order to get about 7–8 grams of dry crystals one should take about 7 grams of caustic potash.

List of Metallic Salts a knowledge of the preparation of which is required in the Conjoint Boards' Syllabus.

### A. SALTS OF INORGANIC ACIDS.

		Salts which can be prepared by a similar method.
Nitrates	Potassium nitrate, $\text{KNO}_3$ Barium nitrate, $\text{Ba}(\text{NO}_3)_2$ Lead nitrate, $\text{Pb}(\text{NO}_3)_2$	$\text{NaNO}_3$ $\text{Ca}(\text{NO}_3)_2$ $\text{Cu}(\text{NO}_3)_2$ , $\text{Hg}(\text{NO}_3)_2$ , $\text{Zn}(\text{NO}_3)_2$ , $\text{Mg}(\text{NO}_3)_2$
Iodide	Lead iodide, $\text{PbI}_2$	$\text{PbCl}_2$
Chloride	Ammonium chloride, $\text{NH}_4\text{Cl}$	$\text{NaCl}$ , $\text{KCl}$ , $\text{CaCl}_2$ , $\text{SrCl}_2$ , $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
Sulphates	Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Ferrous „ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

### B. SALTS OF ORGANIC ACIDS.

Acetate	Lead acetate, $(\text{CH}_3 \cdot \text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$	$(\text{H} \cdot \text{COO})_2\text{Pb}$ . Lead formate.
Oxalate	Ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$	$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$
Tartrates	Potassium hydrogen tartrate, $\text{KH} \cdot \text{C}_4\text{H}_4\text{O}_6$	$\text{KHSO}_4 : \text{NaHSO}_4 :$ $\text{NH}_4\text{HSO}_4 : \text{KH} \cdot \text{C}_2\text{O}_4$
	Potassium antimonyl tartrate, $\text{K} \cdot \text{SbO} \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$	

### Additional Preparations.

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . Sodium sulphate (Glauber's salts).  
 $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . Sodium phosphate (Disodium hydrogen phosphate).  
 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . Borax.  
 $\text{NaHCO}_3$ . Sodium bicarbonate (Baking soda).  
 $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . Sodium carbonate (Washing soda).  
 $\text{KBr}$ . Potassium bromide (cf.  $\text{NaBr}$ ,  $\text{KI}$ ,  $\text{NaI}$ ).  
 $\text{HgI}_2$ . Mercuric iodide.  
 $\text{Cu}_2\text{Cl}_2$ . Cuprous chloride.  
 $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  } Potash alum {  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ .  
or  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  } „ „ { Ammonia alum.



**Oxides of metals:—** $\text{Fe}_2\text{O}_3$  :  $\text{HgO}$  :  $\text{CuO}$  :  $\text{Cu}_2\text{O}$ .

**Hydroxides of metals:—**NaOH. Sodium hydroxide) (also KOH,  
Caustic soda } Caustic potash)

$$\text{Pb(OH)}_2 : \text{Bi(OH)}_3 : \text{Zn(OH)}_2 : \text{Fe(OH)}_3 :$$
$$\text{Al(OH)}_3 : \text{Ca(OH)}_2.$$

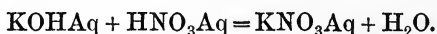
**POTASSIUM NITRATE,  $\text{KNO}_3$**  (cf. p. 52).

**Chemicals required:**—Nitric acid and either caustic potash or potassium carbonate.

(a) **Preparation from Potassium Hydroxide and Nitric Acid.** Dissolve in water 5–8 grams of potassium hydroxide in a small beaker or porcelain dish and neutralize carefully by addition of nitric acid in the following manner. Add nitric acid with frequent stirring until the reaction-mixture is nearly neutral to litmus paper. Do not put the litmus into the solution as it would tint the fluid and spoil the appearance of the crystals. Take out a drop of the solution from time to time by means of a glass-stirring rod and place on litmus paper. When nearly neutral raise the solution to boiling-point and boil for a minute to expel carbon dioxide which might be present. Test again with litmus paper. If the solution be acid add a few drops of potash solution until neutral, and if the solution be alkaline add a few drops of acid until neutral. [NOTE.—It would be preferable to have a drop of acid in excess rather than potash.]

When the solution is quite neutral filter so as to get rid of dust particles, and evaporate down to crystallization. The evaporation should not be too rapid towards the end. To know when to stop evaporating pour about one c.c. into a test-tube, and cool under the tap. From the quantity of solid which separates when the solution has reached room temperature, consider whether it would be worth while stopping the evaporation. The solution must not set quite solid on cooling, but an aqueous sludge would do quite well. If the liquid has been evaporated down too far, add a few c.c. of water, heat up until solution is effected, and then allow to cool. A crust of crystals generally begins to form round the edges of the liquid towards the end of the evaporation, but this is an unreliable guide, as also is the removal of a few drops of liquid on a rod. When sufficiently evaporated cover the dish or beaker with a filter pad and place on a bad

conductor, such as a filter pad or a few folds of paper, so as to ensure slow cooling. When quite cold pour off the supernatant liquid, allowing the liquid to drain away from the crystals as far as possible. Carefully push the crystals out of the dish on to a porous plate or filter pad by means of a spatula. Move the crystals about, but be careful not to break them, and when nearly dry remove to filter paper. When quite dry remove to a dry clock-glass and label them if they are to be shown up, otherwise they might be kept in a test-tube. The equation expressing the reaction would be:



(b) **Preparation from Potassium Carbonate and Nitric Acid.** Put about 10–12 c.c. of concentrated nitric acid in a basin, add about twice the bulk of water, warm gently and slowly, add potassium carbonate in small quantities as long as effervescence continues. Then heat to boiling, boil for a few minutes to expel carbon dioxide which would in solution as carbonic acid have an acid reaction, and then test by putting a drop on filter paper. If acid add more potassium carbonate, if alkaline more nitric acid. When neutral, filter if necessary and evaporate to crystallization. Then proceed as in the preparation from potassium hydroxide and nitric acid.



NOTE.—The directions given in this preparation regarding filtering before evaporation, and the general method of procedure in cooling slowly so as to obtain large crystals, apply to all the succeeding preparations. The directions regarding neutralization apply to all preparations where neutralization is required.

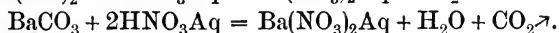
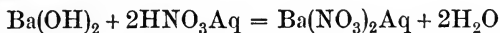
### BARIUM NITRATE, $\text{Ba}(\text{NO}_3)_2$ .

Chemicals required:—Nitric acid and barium hydroxide or barium carbonate.

Put in a beaker or dish 10–15 c.c. of concentrated nitric acid and dilute with about double the bulk of water. Warm, and add slowly the barium hydroxide or barium carbonate until the solution is neutral. This would be indicated approximately in the case of the carbonate by the stoppage of effervescence on adding a fresh quantity, and also by the milkiness of the liquid, as barium carbonate is insoluble in water. Finish the neutraliza-

tion in a similar way to that described under potassium nitrate (i. e. neutralize when boiling), filter if necessary, and evaporate to crystallization. The most suitable time for stopping the evaporation can be best tested by pouring about one c.c. of the boiling liquid into a test-tube, and cooling under the tap. The quantity in the test-tube can be returned to the main bulk of liquid.

Equations:



NOTE.—Calcium nitrate,  $\text{Ca(NO}_3)_2$ , and strontium nitrate,  $\text{Sr(NO}_3)_2$ , can be prepared by similar methods.

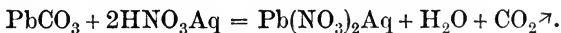
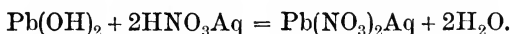
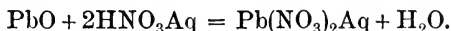
### LEAD NITRATE, $\text{Pb(NO}_3)_2$ .

Chemicals required:—

(a) Nitric acid and lead oxide, hydroxide, or carbonate,  
or (b) Nitric acid and metallic lead.

(a) The preparation of lead nitrate from lead oxide, hydroxide, or carbonate is exactly similar to that described above. Heat up to boiling point in a basin or beaker about 40 c.c. of nitric acid of moderate concentration (one of strong acid to 2 or 3 of water). Then add lead oxide (litharge), hydroxide, or carbonate as long as solution occurs. Boil well before adding more if any seems to remain undissolved. The solution may become alkaline if the liquid is boiled for some time with lead oxide or hydroxide, and this must be avoided, as alkaline solutions of lead nitrate do not crystallize properly. In such a case add a small quantity of acid so as to make the end reaction faintly acid rather than alkaline, filter and evaporate to crystallization. The proper time to stop evaporating should be gauged by cooling a small quantity in a test-tube.

Equations:

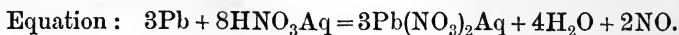


The crystals are nodular in form as a rule.

(b) Preparation from Nitric Acid and Metallic Lead.

The lead should be in such a form that as large a surface as possible is exposed to the action of the acid. Lead foil would do

fairly well. Cut the lead into small pieces and add to the boiling acid. Boil as long as solution continues, filter and evaporate to crystallization.



NOTE. Copper nitrate,  $\text{Cu}(\text{NO}_3)_2$ , mercuric nitrate,  $\text{Hg}(\text{NO}_3)_2$ , zinc nitrate,  $\text{Zn}(\text{NO}_3)_2$ , magnesium nitrate,  $\text{Mg}(\text{NO}_3)_2$ , may be prepared by analogous methods. Oxide, hydroxide, carbonate, or metal can be used except in the case of mercury. Mercury hydroxide and carbonate are not met with.

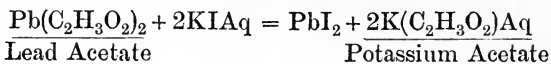
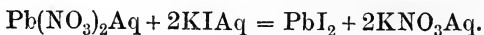
### LEAD IODIDE, $\text{PbI}_2$ .

**Chemicals required :—**A soluble lead salt such as the nitrate or acetate ; potassium iodide.

**Method of procedure :—**Make a moderately strong solution of the soluble lead salt, add a few drops of acetic acid, and then add a solution of potassium iodide as long as a precipitate forms.

NOTE.—The precipitate must be of a deep orange yellow colour. If it is light yellow a basic salt has been formed : a sufficiency of potassium iodide and a small quantity of acetic acid will usually alter the yellow colour to orange. Allow the precipitate to settle, pour off the supernatant liquid, and wash the yellow precipitate twice by decantation. To wash by this process add 50–100 c.c. of distilled water to the precipitate, stir up, allow the precipitate to settle, and then pour off the supernatant liquid. Re-crystallize the product from boiling water. Add a quantity of water, boil, and while boiling continue slowly the addition of water until nearly the whole of the precipitate has dissolved. Then filter the boiling solution if necessary (i.e. if there seems to be a quantity of substance undissolved), and allow to crystallize. Characteristic golden yellow spangles should be obtained.

Equations :



NOTE.—If metallic lead, oxide of lead (litharge), or the carbonate be given as starting-point, prepare a solution of the nitrate, being careful to make the solution nearly neutral before adding the

potassium iodide solution, otherwise iodine may be set free and the preparation spoiled.

**Additional Preparation:**—Lead chloride can be prepared in an exactly similar manner by adding hydrochloric acid to a solution of a lead salt.

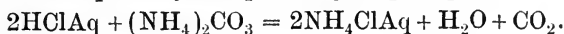
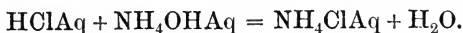


### AMMONIUM CHLORIDE, $\text{NH}_4\text{Cl}$ .

**Chemicals required:**—Hydrochloric acid and either ammonium hydroxide or ammonium carbonate.

**Method of procedure:**—Put into a porcelain dish or small beaker about 20 c.c. of concentrated hydrochloric acid. Add ammonium hydroxide or ammonium carbonate until the reaction is nearly neutral, then heat to boiling, carefully finish the neutralization, filter if necessary, and evaporate to crystallization. The substance is fairly soluble in water, so that the solution must be evaporated down to a considerable extent. Test a small quantity by cooling before stopping the evaporation of the whole.

Only small crystals can be obtained under ordinary conditions, but the mass obtained ought to be distinctly crystalline throughout.



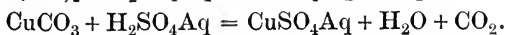
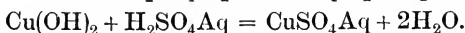
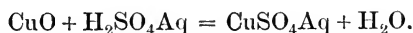
**Additional Preparations:**—Many other chlorides, e.g. those of sodium, potassium, calcium, strontium, and barium, can be obtained by analogous reactions.

### COPPER SULPHATE, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Blue Vitriol).

**Chemicals required:**—Metallic copper, copper oxide, copper hydroxide, or copper carbonate and sulphuric acid.

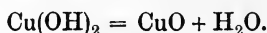
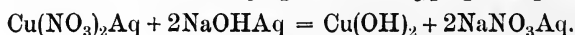
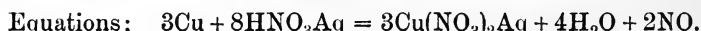
(a) **Preparation from Oxide, Hydroxide, or Carbonate.** Heat about 50 c.c. of dilute sulphuric (one of conc. acid to about 8 of water) in a dish, and then slowly add small quantities of the copper compound until no more dissolves on boiling for say 10 minutes; filter and evaporate carefully to crystallization.

Equations:



(The carbonate would probably be a basic salt, p. 50.)

(b) **Preparation from Metallic Copper.** If copper be given as the starting-point, the best plan is to first prepare copper oxide from it. This can be readily effected by dissolving the copper in a sufficiency of nitric acid, adding excess of caustic soda or potash, and boiling. A black precipitate of copper oxide is obtained. Allow to settle, decant off the supernatant liquid, and wash by decantation. Then dissolve in dilute sulphuric acid, filter, and evaporate to crystallization.

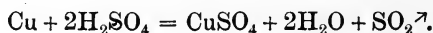


**Alternative Methods of preparation from the metal.**

(i) After solution in nitric acid, the solution may be evaporated to dryness and ignited, when copper oxide would be formed, and should be dissolved in dilute acid.



(ii) Dissolve the metal in a sufficiency of concentrated sulphuric acid with a few drops of concentrated nitric acid in a fume cupboard, dilute with water, boil, filter and evaporate to crystallization.



NOTE.—This method is not a convenient one.

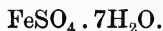
### **FERROUS SULPHATE, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Green Vitriol).**

Take 10–12 grams of iron filings in a flask or basin and boil up with dilute sulphuric acid (1 in 5 or 6) as long as hydrogen is evolved, keeping the filings in slight excess. Filter and evaporate to crystallization.

When the crystals have separated, decant the supernatant fluid, and dry the crystals on a filter pad or plate.

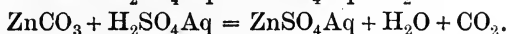
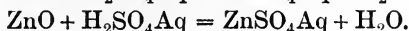
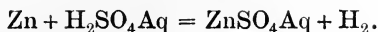


The green crystals which separate have the composition



**Additional Preparations:—**Zinc sulphate (White Vitriol) may be prepared in the same way, or may be obtained by heating dilute sulphuric acid in a dish and adding zinc oxide or zinc carbonate as long as solution takes place, then filtering and evaporating.

Equations :



Magnesium sulphate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) may be prepared in a similar manner to zinc sulphate.

### ORGANIC COMPOUNDS.

(1) **LEAD ACETATE** (Sugar of Lead).  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ ,  
or  $(\text{CH}_3 \cdot \text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ .

**Chemicals required:**—Lead oxide or carbonate and acetic acid.

**Method of procedure:**—Dilute 10–15 c.c. of glacial acetic acid with about twice its bulk of water, heat to boiling in a porcelain dish, and then add the lead oxide or carbonate as long as it seems to dissolve, then filter, make distinctly acid with acetic acid and evaporate to crystallization. It must be noted that lead acetate is one of those compounds which tend to become supersaturated upon evaporation.

[NOTE:—A solution is said to be supersaturated when it retains in solution more than corresponds to the normal saturated state for the given temperature. On adding a crystal of the solute to a supersaturated solution the substance separates rapidly.]

If after evaporating to a small bulk no solid begins to separate, pour about one c.c. into a test-tube, cool well and stir thoroughly with a glass rod. If a crop of crystals separates, allow the rest of the solution to cool and then add the crystals. The solution generally crystallizes. If, as is sometimes the case, the whole sets to a solid mass, keep a few crystals of this mass, dissolve the rest in the minimum quantity of boiling water, and cool. If crystals do not separate, add those which were removed, and crystallization will generally ensue.

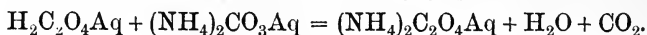
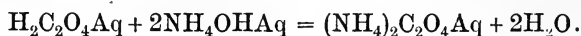
(2) **AMMONIUM OXALATE**,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ .

**Chemicals required:**—Ammonium hydroxide or carbonate and oxalic acid.

Dissolve about 5 grams of oxalic acid in water and add ammonia solution or ammonium carbonate until the reaction is neutral or faintly alkaline. Heat to boiling before finishing

neutralization if ammonium carbonate is used. Filter the solution to free from dust particles, if necessary, and evaporate to crystallization. Large well-developed crystals should be obtained if the solution is allowed to cool slowly.

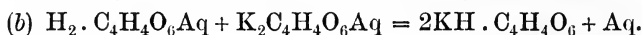
Equations:



### (3) POTASSIUM HYDROGEN TARTRATE, $\text{KH} \cdot \text{C}_4\text{H}_4\text{O}_6$ .

Dissolve about 10 grams of tartaric acid in approximately 50 c.c. of water, shake or stir well so as to get a homogeneous solution, divide into 2 equal parts and neutralize one half exactly by means of potassium hydroxide or potassium carbonate. Finish the neutralization after boiling to decompose any carbonic acid in solution. Then add the other half of the tartaric acid. A thick precipitate of potassium hydrogen tartrate generally comes down. Cool thoroughly, decant off the supernatant liquid, and recrystallize the potassium hydrogen tartrate by dissolving in the proper quantity of boiling water and cooling slowly. Decant and dry as usual.

Equations:—

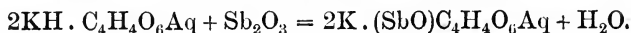


**Additional Preparations:**—Potassium hydrogen sulphate,  $\text{KHSO}_4$ , sodium hydrogen sulphate,  $\text{NaHSO}_4$ , ammonium hydrogen sulphate,  $\text{NH}_4 \cdot \text{HSO}_4$ , and potassium hydrogen oxalate,  $\text{KH} \cdot \text{C}_2\text{O}_4$ , may all be similarly prepared.

### (4) POTASSIUM ANTIMONYL TARTRATE (Tartar Emetic),



Dissolve about 5 grams of potassium hydrogen tartrate in boiling water, and add gradually to the solution small quantities of antimonious oxide ( $\text{Sb}_2\text{O}_3$ ). About 4 grams should be roughly weighed out and added slowly with constant boiling; filter and evaporate to crystallization. Determine when to stop evaporating by cooling a small quantity in a test-tube in the usual way.



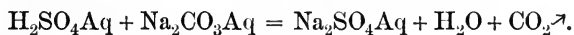
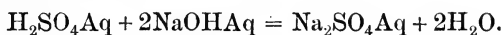


## ADDITIONAL PREPARATIONS.

**SODIUM SULPHATE** (Glauber's Salt),  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

**Method:**—Neutralize about 50 c.c. of dilute sulphuric acid with sodium hydroxide or carbonate, filter if necessary, and evaporate to crystallization.

**Equations:**



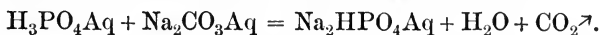
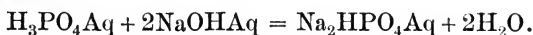
Large efflorescent crystals are obtained.

Potassium sulphate,  $\text{K}_2\text{SO}_4$ , and ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ , may be prepared by analogous methods.

**DISODIUM HYDROGEN PHOSPHATE** (Common Sodium Phosphate),  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ .

**Method:**—Neutralize a boiling solution of phosphoric acid with sodium hydroxide or sodium carbonate, filter, and evaporate carefully to crystallization.

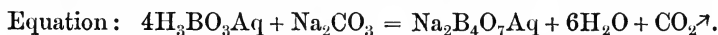
**Equations:**



As already mentioned (p. 50), common sodium phosphate is an acid salt, but is nearly neutral in reaction.

**SODIUM PYROBORATE** (Sodium Tetraborate), **BORAX**,  
 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

Dissolve about 3 grams of boracic acid in boiling water, neutralize with sodium carbonate, filter, and evaporate to crystallization.



The orthoborates (salts of boracic or boric acid) are unstable. Borax is a salt of tetraboric or pyroboric acid,  $\text{H}_2\text{B}_4\text{O}_7$ .

**SODIUM BICARBONATE** (Baking Soda),  $\text{NaHCO}_3$ , and **SODIUM CARBONATE**: (a) anhydrous,  $\text{Na}_2\text{CO}_3$ ; (b) hydrated (Washing Soda),  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ .

On passing carbon dioxide through a solution of caustic soda, sodium carbonate is first obtained, and then, with excess of carbon dioxide, sodium bicarbonate is formed. It should be noted that this is a general type of reaction. The normal salt is first formed, and then, if more acid be added, the acid salt

can be obtained (cf. preparation of  $\text{KH} \cdot \text{C}_4\text{H}_4\text{O}_6$ , p. 64). In this case one adds an acid anhydride, which, with water, forms carbonic acid.

**Method:**—Dissolve about 6 grams of caustic soda in 20 c.c. of water and pass carbon dioxide (prepared from marble and hydrochloric acid, p. 39) into the solution until no further absorption seems to take place. A precipitate of sodium bicarbonate will probably be thrown down. Evaporate to dryness in a porcelain dish and then heat the residue. Sodium carbonate will be obtained. The anhydrous product may be dissolved in water and crystallized, when efflorescent crystals of the decahydrated salt will be formed.

Equations:  $2\text{NaOHAq} + \text{CO}_2 = \text{Na}_2\text{CO}_3\text{Aq} + \text{H}_2\text{O}$ .

$\text{Na}_2\text{CO}_3\text{Aq} + \text{CO}_2 + \text{H}_2\text{O} = 2\text{NaHCO}_3\text{Aq}$ .

On heating  $2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$ .

**NOTES:**—(a) Potassium bicarbonate,  $\text{KHCO}_3$ , and potassium carbonate,  $\text{K}_2\text{CO}_3$ , can be similarly prepared.

(b) By using sulphur dioxide instead of carbon dioxide we can obtain sodium and potassium bisulphites and sulphites analogously:— $\text{NaHSO}_3$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{KHSO}_3$ , and  $\text{K}_2\text{SO}_3$ .

### POTASSIUM BROMIDE, $\text{KBr}$ .

Dissolve about 6 grams of potassium hydroxide in 40–50 c.c. of water, and then add about 9 grams of bromine (3 c.c. approximately) with constant stirring until the liquid is tinted faintly yellow. [Caution. Be careful not to inhale bromine vapour, and note that bromine causes very painful burns.] Evaporate down to dryness, when a mixture of potassium bromide and potassium bromate will be obtained. Powder the residue in a mortar with about an equal weight of wood charcoal, remove to a crucible, and heat over a Bunsen burner for about fifteen minutes. The bromate is decomposed. Allow to cool, remove to a beaker containing about 50 c.c. of water, boil for a few minutes, filter off the excess of carbon, and evaporate to crystallization in a porcelain dish.

Equations:

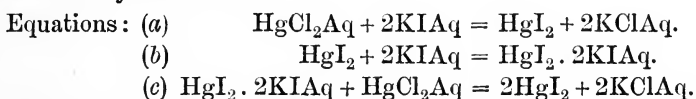
(a)  $6\text{KOHAg} + 3\text{Br}_2 = \text{KB}_3\text{O}_8\text{Ag} + 5\text{KBrAg} + 3\text{H}_2\text{O}$ .

(b)  $\text{KBrO}_3 + 3\text{C} = \text{KBr} + 3\text{CO} \nearrow$ .

**NOTE:**—Sodium bromide,  $\text{NaBr}$ , potassium iodide,  $\text{KI}$ , and sodium iodide,  $\text{NaI}$ , can be prepared by exactly similar methods.

**MERCURIC IODIDE,  $\text{HgI}_2$ .**

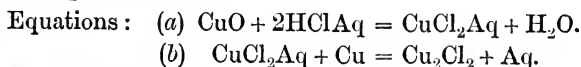
Take about 20 c.c. of a concentrated solution of mercuric chloride in water, and divide into two equal portions. To one half, add a concentrated solution of potassium iodide until the precipitate which first forms nearly redissolves, and then add the other half of the mercuric chloride solution. A scarlet precipitate of mercuric iodide will be obtained. Allow to settle, pour off the supernatant liquid, wash once by decantation, and then recrystallize the residue from concentrated hot hydrochloric acid. Allow the crystals to settle, pour off the hydrochloric acid, and then dry the residue.



Equation (b) indicates that the mercuric iodide first precipitated redissolves to form a double compound containing as much potassium iodide as was required for the precipitation.

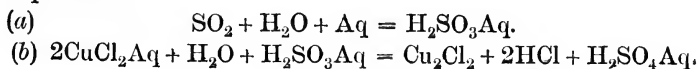
**CUPROUS CHLORIDE,  $\text{Cu}_2\text{Cl}_2$ .**

**Method I.** Put about 5 grams of copper oxide and 5 grams of copper turnings in a flask, add 100 c.c. of concentrated hydrochloric acid, and boil up gently for about half an hour in the fume cupboard. A funnel should be loosely placed in the neck of the flask so as to retard loss of hydrochloric acid. The copper oxide with hydrochloric acid will form cupric chloride ( $\text{CuCl}_2$ ), which will be reduced by the copper present to form cuprous chloride, which is soluble in hydrochloric acid, but insoluble in water. When the solution is nearly colourless, pour into about 100 c.c. of water, and a white precipitate of cuprous chloride will at once form. Filter, dry, and keep in a sealed tube, or in a small bottle the stopper of which is afterwards covered with melted paraffin wax.



**Method II.** Cuprous chloride can also be prepared by passing sulphur dioxide into a solution of cupric chloride. The cuprous chloride comes down as a white crystalline precipitate.

Equations:

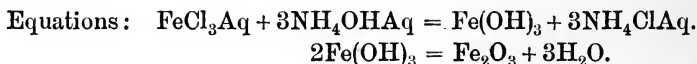


[Potash alum,  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$  or  $KAl(SO_4)_2 \cdot 12H_2O$ , can be prepared by mixing molecular proportions of potassium sulphate and aluminium sulphate in solution and evaporating to crystallization, preferably at a low temperature. Note:—Ammonia alum,  $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ , can be prepared similarly.]

## B. PREPARATION OF A FEW TYPICAL OXIDES.

### FERRIC OXIDE, $Fe_2O_3$ .

Add ammonium hydroxide to a warm solution of ferric chloride as long as a precipitate forms, filter off the brown precipitate of ferric hydroxide, dry in an air oven at about  $100^\circ C$ ., remove from the filter paper or cloth, powder, and heat gently in a dish or crucible. The ferric oxide is obtained as a reddish powder.



NOTE:—Aluminium oxide,  $Al_2O_3$ , bismuth oxide,  $Bi_2O_3$ , chromium oxide,  $Cr_2O_3$ , and lead oxide,  $PbO$ , could be prepared by exactly similar processes.

### MERCURIC OXIDE, $HgO$ .

There are two varieties—(a) yellow, (b) red.

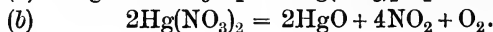
(a) **Preparation of yellow Mercuric Oxide.** Dissolve a few grams of mercuric chloride in water and then add sodium or potassium hydroxide solution as long as a precipitate forms. Filter the yellow precipitate, dry, and powder it.



NOTE:—Mercurous oxide,  $Hg_2O$ , can be obtained as a black powder in a similar way from mercurous nitrate solution ( $HgNO_3Aq$ ).

(b) **Preparation of red Mercuric Oxide.** Dissolve a few grams of mercury in moderately concentrated nitric acid, evaporate the solution of mercuric nitrate to dryness, and heat cautiously. A nearly black residue is left, which turns red on cooling.

Equations :

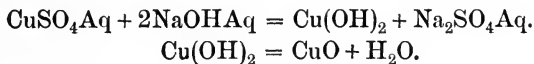


NOTE:—Cupric oxide,  $CuO$ , can be prepared by an analogous process from metallic copper.

**CUPRIC OXIDE, CuO.**

Copper oxide can also be obtained by adding excess of caustic alkali (soda or potash) to a solution of a copper salt, boiling, filtering, washing, and finally drying and heating the black precipitate obtained. A blue precipitate of the hydroxide is first thrown down, but this decomposes on boiling to give oxide and water.

Equations:

**CUPROUS OXIDE, Cu<sub>2</sub>O.**

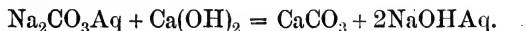
Dissolve 3–5 grams of crystallized copper sulphate in about 100 c.c. of cold water. Add to the solution caustic soda or potash until the reaction just becomes alkaline. A blue precipitate of cupric hydroxide will form. Add 5–10 per cent. glucose solution with constant stirring until the precipitate just dissolves to give a deep blue solution. Boil for a few minutes. A deep red precipitate of cuprous oxide comes down. Filter and wash.

**PREPARATION OF HYDROXIDES.**

The hydroxides of Na, K, NH<sub>4</sub> are easily soluble in water and those of Ca, Sr, and Ba are moderately soluble. All the others are insoluble in water and can be obtained by precipitation.

**(1) SODIUM HYDROXIDE, CAUSTIC SODA, NaOH.**

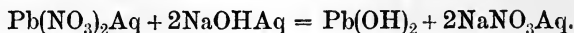
Make a dilute solution of sodium carbonate by dissolving about 5 grams of the crystallized substance in 80–100 c.c. of water. Then add milk of lime gradually with constant stirring to the warm solution until, after allowing any precipitate to settle, it is found that a small test quantity of the solution does not effervesce with hydrochloric acid. Filter and evaporate nearly to dryness in an iron or silver dish: strong caustic soda solution attacks glass and porcelain.



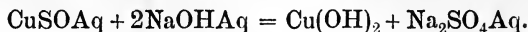
NOTE:—Potassium hydroxide (caustic potash), KOH, can be prepared in a similar manner.

Prepare the following Hydroxides in a test-tube by adding NaOHAq, KOHAq, or NH<sub>4</sub>OHAq to a soluble salt of the metal.

- (2) **Lead Hydroxide,  $\text{Pb}(\text{OH})_2$ .** White solid.

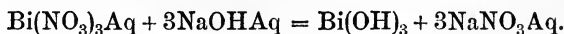


- (3) **Copper Hydroxide,  $\text{Cu}(\text{OH})_2$ .** Blue solid.

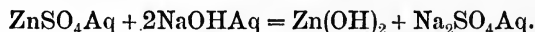


Avoid adding excess of  $\text{NaOHAq}$  and do not heat.

- (4) **Bismuth Hydroxide,  $\text{Bi}(\text{OH})_3$ .** White solid.

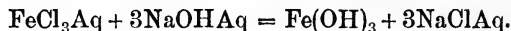


- (5) **Zinc Hydroxide,  $\text{Zn}(\text{OH})_2$ .** White solid.

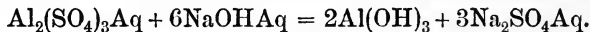


Do not add excess of  $\text{NaOHAq}$ , as the precipitate is soluble in excess.

- (6) **Ferric Hydroxide,  $\text{Fe}(\text{OH})_3$ .** Reddish brown solid.



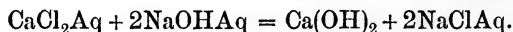
- (7) **Aluminium Hydroxide,  $\text{Al}(\text{OH})_3$ .** White gelatinous solid.



Do not add excess of  $\text{NaOHAq}$ , as the precipitate is soluble in excess.

- (8) **Calcium Hydroxide, Slaked Lime,  $\text{Ca}(\text{OH})_2$ .** White solid.

To a concentrated solution of calcium chloride add  $\text{NaOHAq}$ .



NOTE:—All the above hydroxides can be filtered off and dried at  $100^\circ \text{C}$ . in air bath without decomposition, with the exception of the hydroxides of iron and aluminium, which lose water and form oxides.

## MEMORANDA

## MEMORANDA



## PART III

### TESTS FOR ELECTRO-POSITIVE RADICLES

- A. Dry Tests for the Metals
- B. Wet Tests for the Metals
- C. Complete Summary of both Wet and Dry Tests  
for the Metals



## PART III

### TESTS FOR ELECTRO-POSITIVE RADICLES

A. Dry Tests for the Metals.

B. Wet Tests for the Metals.

C. Complete Summary of both Wet and Dry Tests for the Metals.

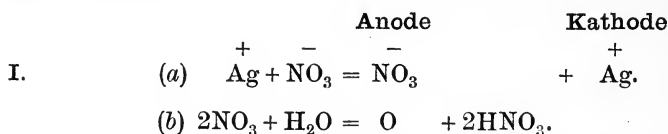
Detection of the Metals—the Electro-positive Radicles or Kations.

The metals are frequently termed **electro-positive radicles** or **kations**, and the **acid radicles** (e.g.  $\text{NO}_3$ ,  $\text{SO}_4$ ,  $\text{Cl}$ ), **electro-negative radicles** or **anions**. These terms may be explained by the following considerations.

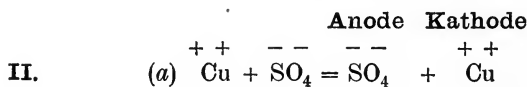
If one passes an electric current through solutions of (*a*) silver nitrate, (*b*) copper sulphate, using say a few cells to supply the current and strips of platinum as electrodes, metal is set free at the **kathode**—the electrode at which the current leaves the electrolytic cell—and **oxygen** at the **anode**—the electrode at which the current enters the cell. These facts are best explained by the **Ionization Hypothesis**. This hypothesis assumes that all acids, bases, and metallic salts in solution in water are dissociated\* more or less completely into small particles carrying electrical charges called ions. These ions may be single atoms or groups of atoms; e.g. copper sulphate in dilute solution in water consists chiefly of ions of copper with positive charges of electricity, and sulphion ions ( $\text{SO}_4$ ) with negative charges of electricity.

\* The distinction between dissociation and ordinary decomposition should be noted. Dissociation is a term applied to the splitting up of a body into radicles which recombine readily under ordinary conditions, whereas in true decomposition this recombination does not occur. Electrolytic and Thermal Dissociation are met with.

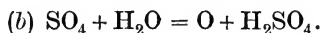
On placing such solutions in an electrical circuit using suitable electrodes, since **Like charges of electricity repel and Unlike charges attract**, the **negatively charged ions** will move over to the electrode connected with the positive pole of the battery (the **anode**), and the **positively charged ions** will move over to the electrode connected with the negative pole of the battery (the **kathode**). In the case of copper sulphate the sulphion ion being the negatively charged ion will be set free at the anode, and the positively charged copper ion moves to the kathode. The sulphion ion, on reaching the anode and giving up its charge, reacts with water, forming oxygen and sulphuric acid, while the copper ions stick to the kathode, forming a deposit of metallic copper. What takes place in each case might be represented by two equations:—



The  $\text{NO}_3$  ion (which is unknown in the free state) reacts with water to give oxygen, which comes off as gas and  $\text{HNO}_3$ , which remains in solution round the anode.



(NOTE:—The divalent ions are represented as having double the electrical charges of the monovalent ions.)

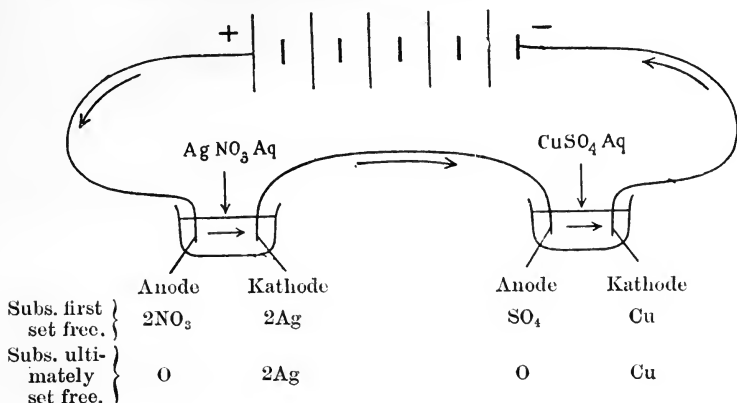


The  $\text{SO}_4$  ion is unknown in the free state. On giving up its electrical charge it reacts with water to give oxygen and sulphuric acid.

The metals in solutions of salts always move to the kathode and the acid radicles to the anode. In the case of acids, hydrogen moves to the kathode and acid radicles move to the anode, and in the case of soluble bases, metals to the kathode and hydroxyl ions to the anode. One might therefore say that **hydrogen and the metals are electro-positive radicles or kations**, and **oxygen, chlorine, acid radicles** (i.e. acid-less hydrogen), e.g.  $\text{NO}_3$ ,  $\text{SO}_4$ ,

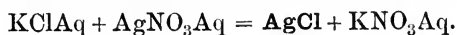
$\text{Fe}(\text{CN})_6$ , and hydroxyl  $\text{OH}$  are electro-negative radicles or anions.

The following diagram summarizes what has been stated above.

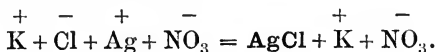


The above facts must be clearly grasped before the lists of tests given in the following pages are properly understood. The interactions are as a rule ion reactions. The precipitates formed are un-ionized bodies insoluble under the given conditions. A few examples may make the relationships clear.

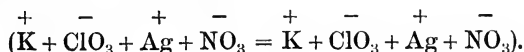
1. If one adds silver nitrate solution to potassium chloride, a white precipitate of un-ionized silver chloride is formed, the reaction being most conveniently represented by the equation :



Written from the ionic point of view :



Other soluble chlorides, e.g.  $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ , would react in a similar manner, and one might suppose that any metallic compound containing chlorine would behave in the same way. This is not the case.  $\text{AgNO}_3\text{Aq}$  is a reagent for the ion chlorine, and gives no reactions with bodies like potassium chlorate ( $\text{KClO}_3$ ), where the chlorine forms part of a complex radicle. If one attempts to write an equation in this case the two sides would be identical.

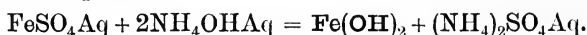


Silver chlorate is soluble in water, and therefore ionized, and no precipitate forms.

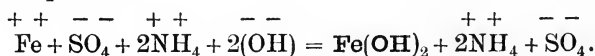
2. Ferrous and ferric salts give a precipitate of ferrous and ferric hydroxides with ammonium hydroxide, and one might suppose that all iron compounds should give a precipitate with  $\text{NH}_4\text{OH}$ . This would be quite an erroneous assumption, as could easily be proved by adding  $\text{NH}_4\text{OH}$  to potassium ferrocyanide or potassium ferricyanide, when no precipitate would form. Ammonium hydroxide is merely a reagent for ferrous and ferric ions, and the precipitation of ferrous and ferric hydroxides from ferrous sulphate and ferric chloride respectively might be represented by the following equations:—

(a) Precipitation of Ferrous Salts.

Ordinary equation :

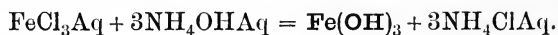


Ionic equation :

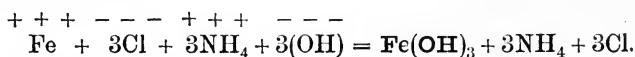


(b) Precipitation of Ferric Salts.

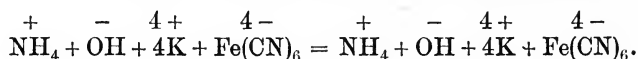
Ordinary equation :



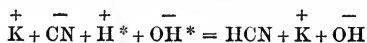
Ionic equation :



With  $\text{NH}_4\text{OH}$  and potassium ferrocyanide nothing occurs :



[It might be pointed out that many peculiar phenomena difficult to understand otherwise are readily explained by the ionic theory. For example, potassium cyanide in solution is strongly alkaline in reaction. This follows because the body reacts with water to give un-ionized hydrocyanic acid and ionized potassium hydroxide.



Free hydroxyl ions are present in quantity, and therefore the body is alkaline in reaction, as free hydroxyl ions cause alkalinity.

\* Water is only very slightly ionized into H and OH.

Similarly, certain normal salts in solution (e. g.  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ) have an acid reaction, because of presence of free hydrogen ions which cause acidity.

Many other phenomena, e. g. abnormal depression of freezing-point and abnormal raising of boiling-point, can also be explained.]

Throughout this book ordinary equations are used, as ionic equations are unnecessarily complicated. The above explanations should, however, be kept in view.

## A. DRY TESTS FOR THE METALS.

The dry tests often afford a ready means for identification of a metal, and are particularly useful when the substance is soluble with difficulty.

The more important dry tests comprise:—

- (1) Reduction of metals on charcoal.
- (2) (a) Coloured residues obtained on ignition of filter paper saturated with the metallic salt and cobalt nitrate.
- (b) Coloured masses on charcoal.
- (3) Coloured incrustations around the heated area.
- (4) Borax bead tests.
- (5) Platinum wire tests—flame tests.

For all these tests a reducing or oxidizing flame is required. A reducing flame is one containing white-hot carbon, and is therefore generally luminous, while an oxidizing flame contains excess of oxygen, and is usually non-luminous.

The **Bunsen flame** is the most convenient for general use. When the holes for admitting air at the base of the tube are open the Bunsen flame has three zones:—

(a) A central zone of unburnt gas mixed with air reaching a short distance above the top of the tube.

[(b) A shallow zone of bluish colour round the inner zone. Partial combustion of the carbon to carbon monoxide takes place here and hydrogen is present, so that the zone would have reducing action. From our point of view this zone need hardly be considered.]

(c) A zone of complete combustion surrounding the other zones and usually reaching to about double the height. To prove these statements as regards zones (a) and (c), after lighting the gas depress a piece of wire gauze until it is about an inch from the mouth of the tube. Note that the wire seems unaltered in the centre of the flame, but becomes red hot in the surrounding zone of complete combustion. The three zones are shown in the accompanying diagram, Fig. 11 (A).



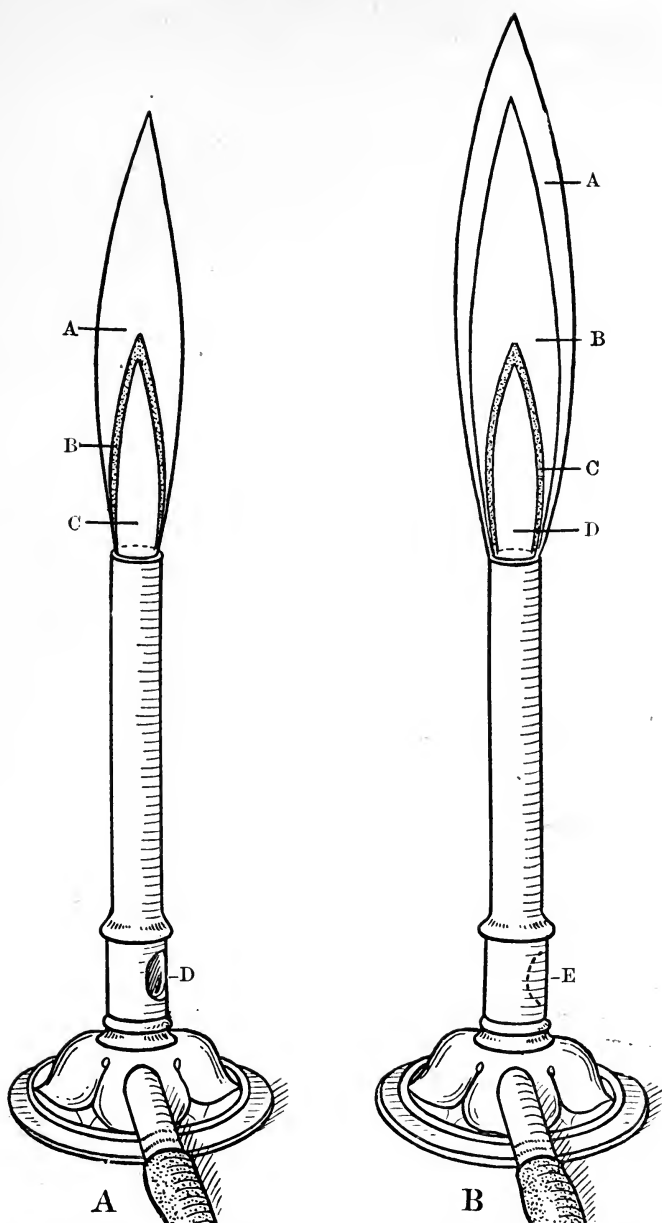


FIG. 11. DIAGRAMMATIC REPRESENTATION OF ZONES OF (A) OXIDIZING FLAME, (B) REDUCING FLAME. A, a, Zone of complete Combustion (Oxidizing); b, Bluish Zone; c, Inner Zone of unburnt Gas admixed with Air; d, Air Entrance. B, a, Zone of complete Combustion (Oxidizing); b, Yellowish Zone containing white-hot Carbon (reducing); c, Bluish Zone; d, Inner Zone of unburnt Gases; e, Opening closed.

**Adjustment of Bunsen burner so as to obtain an oxidizing or reducing flame.**

(a) One method of obtaining a reducing flame is to shut the holes at the bottom of the tube so as to allow no air to mix with the gas. One then gets a smoky yellow flame containing white-hot carbon. Four zones are here present as indicated in Fig. 11 (B).

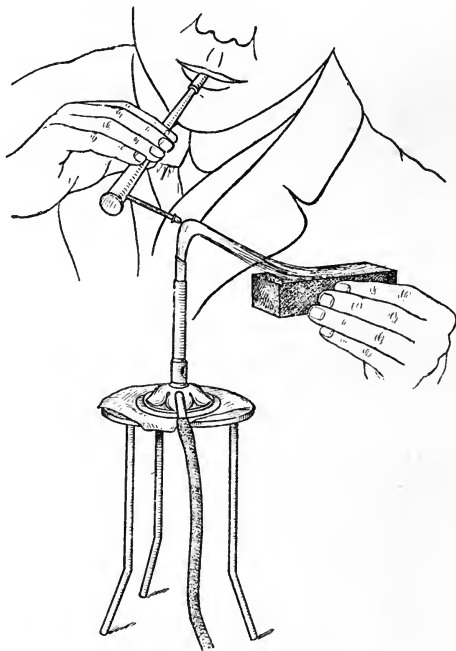


FIG. 12. METHOD OF HEATING METALLIC SUBSTANCE ON CHARCOAL IN REDUCING FLAME.

(b) In order to get an oxidizing flame, open the holes at the bottom as widely as possible so as to admit a maximum supply of air.

(c) To get a flame which is partly reducing and partly oxidizing, close the holes at the bottom until the flame has a luminous tip. The luminous portion would exert reducing action, but above it and at the sides of the flame there would be oxidizing zones.

**(d) Suitable flame for Reduction of Metals.**

Instead of using the Bunsen flame direct, it is more convenient to adapt the flame by means of a mouth blowpipe for the isolation

of metals and for obtaining coloured masses and incrustations. The mouth blowpipe generally consists of a hollow conical tube open at the apex for blowing, and with a nozzle near the base. Close the holes at the bottom of the Bunsen burner so as to get a luminous flame, and then put a metal tube ending in a slit making an angle of about  $50^\circ$  with the horizontal, into the Bunsen tube so as to get a flame convenient to regulate. Adjust the flame until it is  $2\frac{1}{2}$  to  $3\frac{1}{2}$  inches high, and then put the tip of

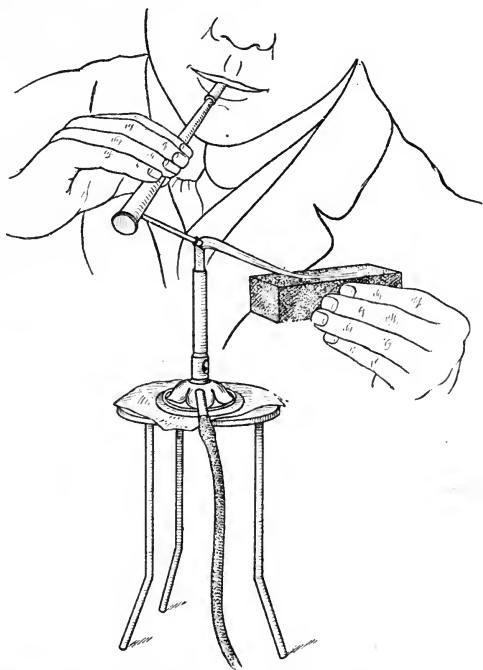


FIG. 13. METHOD OF HEATING A METALLIC COMPOUND ON CHARCOAL IN OXIDIZING FLAME.

the mouth blowpipe about an inch above the upper end of the slit and just outside the flame and blow gently. The luminous reducing flame can be blown downwards in any given direction, as indicated in Fig. 12. The blowing should be done entirely from the cheeks, which should be kept inflated, breathing being carried on through the nostrils. With a little practice it will be found that one can blow steadily for 5 to 10 minutes without stopping.

(e) If an oxidizing flame is wanted, such as gives best results

when trying for coloured masses or incrustations, put the nozzle of the blowpipe into the flame, adapted as described above, and blow fairly strongly. A very hot non-luminous, strongly oxidizing flame is obtained. The proper method is indicated in Fig. 13. In Chemistry, 'Reduction' is a term applied to a general type of reaction, which here means removal of oxygen and other electro-negative elements or groups, to set free the metal.

### 1. REDUCTION ON CHARCOAL.

The Metals may be classed as follows with regard to their reducibility on charcoal:—

(1) Metals reduced from their compounds, some giving beads under proper conditions: Pb, Ag, Cu, Bi, Sb, Sn, Fe, (Mn), (Cr).

(2) Metals reduced and volatilized: As, Hg, (Sb).

Arsenic is oxidized to arsenious oxide on volatilization.

NOTE.—Ammonium compounds are decomposed or volatilized on heating.

(3) Metals not reduced on charcoal: Al, Zn, Mg, Ca, Ba, Na, K.

#### Mode of Procedure:—

Heat up the substance either alone or admixed with about twice its bulk of fusion mixture on a small hollow scraped in block carbon or wood charcoal in the reducing flame as indicated in Fig. 12. Fusion mixture is a mixture of anhydrous powdered sodium carbonate and potassium carbonate. If not obtainable, sodium carbonate alone will do.

#### Results:—

(1) **Lead Compounds** readily yield **Metallic Lead**. No fusion mixture is required. The bead tends to get covered with a yellowish film of oxide as it cools. When the cold bead is examined, it is found to be very malleable and to mark paper.

(2) **Silver** compounds give silver first as a film and then as a brilliant silvery bead. Fusion mixture assists the reaction, but is not absolutely necessary.

(3) **Copper**. In reducing copper compounds mix the powdered substance with fusion mixture and a small quantity of potassium cyanide. [CAUTION.—Potassium cyanide is a very poisonous compound.] Red scales are obtained after heating for some time.

(4) **Bismuth** compounds reduce fairly readily. A brittle bead is obtained.

(5) **Antimony** compounds generally give a brittle bead. On heating the reduced metal it volatilizes, and is oxidized by the oxygen of the air as it passes through the flame, giving a white fume of antimonious oxide which may partly condense on the charcoal outside the heated area.

(6) **Tin** compounds usually reduce with difficulty. Mix the powdered substance with fusion mixture (or borax) and potassium cyanide. A white silvery bead is obtained.

(7) **Iron** compounds usually yield a magnetic residue which can be tested by a magnetized knife-blade.

## II. Reduction in Bulb Tube.

Take a small quantity of dry powdered substance, mix with powdered carbon and a small quantity of fusion mixture, and introduce into a small tube of hard glass, which should preferably be expanded into a small bulb at the closed end. Heat the mixture cautiously.

**Arsenic** compounds (with a few exceptions, e. g.  $\text{As}_2\text{S}_3$ ) give a greyish mirror of arsenic.

NOTE.—If a small quantity of potassium cyanide is added to the above reaction mixture, *all* arsenic compounds will be reduced.

**Antimony** compounds give a similar mirror of antimony.

**Mercury** compounds give a metallic film of mercury. This test for mercury is unimportant as the wet tests for that element are so characteristic, but for arsenic and antimony it is invaluable. The films of arsenic and antimony can be readily distinguished from each other by making a file mark at the base of the mirror, breaking off the tube, and heating up the mirror with bleaching powder solution in a test-tube. The arsenic film dissolves, while that of antimony remains nearly unaffected.

## 2. COLOURED MASSES.

The preparation of coloured masses<sup>m</sup> affords convenient confirmatory tests for zinc, tin, magnesium, and aluminium.

a. If the substance is a solution or soluble in water, or is readily soluble in acid, proceed as follows:—

Pour about 1 c.c. of a concentrated solution of the substance on to say half a filter paper, so as to thoroughly wet a few square centimetres, then pour about the same quantity of cobalt nitrate solution on to the moistened portion of the paper. Incinerate

by holding with tongs in the ordinary Bunsen flame (i. e. oxidizing flame). The following coloured residues are obtained :—

Zinc compounds give a light green residue.

Tin compounds (sometimes with difficulty) give a dark green residue.

Magnesium compounds give a light pink residue.

Aluminium compounds give a bright blue residue.

PRECAUTION.—In connexion with this residue from aluminium compounds it must be observed that phosphates, arsenates, and borates may give a similar blue mass. The blue residue from a pure aluminium compound is infusible, while the others can be fused.

b. If the substance is not readily soluble, proceed as follows :—

Heat a small quantity of the substance in a shallow hollow on charcoal by the oxidizing blowpipe flame. If the residue is white, moisten with cobalt nitrate and reheat. Coloured masses similar to the residues obtained above will be formed.

### 3. COLOURED INCRUSTATIONS AROUND THE HEATED AREA.

Certain metals give characteristic incrustations around the heated area. These are not of primary importance, but they sometimes give a valuable hint, and are therefore worth mentioning.

- (a) Yellow when hot, white when cold indicates **Zinc**.
- (b) Orange when hot, light yellow when cold indicates **Bismuth**.
- (c) Yellow, both hot and cold, indicates **Lead**.
- (d) White fumes with garlic odour indicate **Arsenic**.

The compounds of **Antimony**, **Ammonium**, and **Mercury** may give fumes.

### 4. BORAX BEAD TESTS are often useful.

**Preparation of a Borax bead.** Make an oval loop, about 2 millimetres in length and 1 millimetre in breadth, at the end of a small piece of platinum wire, which should preferably be fused into the end of a glass rod about 4 inches long. Heat the loop and dip it into powdered borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), some of which

will adhere to the wire. Remove the wire and heat in the oxidizing flame. The mass at first froths up, owing to the disengagement of water of crystallization, and finally gives a clear glassy bead. Take a very minute trace of the powdered substance on to the bead by bringing the heated borax carefully into contact with the powder, and heat strongly in the oxidizing flame. It is not necessary to use a blowpipe, but it saves time to do so. In many cases the reducing flame would yield different products, but it is hardly necessary to use it.

**Copper** compounds give blue bead in oxidizing flame (and reddish in reducing flame).

**Iron** compounds give yellowish-brown bead in oxidizing flame (and bottle-green bead in reducing flame).

(**Chromium** compounds give a green bead.)

(**Manganese** compounds give an amethyst coloured, i. e. light violet, bead.)

(**Cobalt** compounds give a deep blue bead.)

To get rid of a bead, heat and dip into water; the bead will break into pieces and can be readily removed. If the bead is too dark it can be brought to a convenient tint by heating, taking up more borax, fusing, shaking off a portion and repeating the process if necessary.

## 5. PLATINUM WIRE TESTS.

These form admirable confirmatory tests, and are easily carried out. A trace of substance is taken on the tip of a platinum wire provided with a glass handle, and carefully introduced near the base of the edge of the flame. The colours depend upon the formation of vapour of metal in the flame zone, and therefore the substance must be volatile at the temperature of the flame. If non-volatile no colour results; e.g. pure copper oxide gives no colour to a Bunsen flame, but if moistened with hydrochloric acid and then introduced the flame is tinted a brilliant green to blue tint, because copper chloride is formed by interaction of the copper oxide and hydrochloric acid, and all chlorides are volatilized in the Bunsen flame.

**Method.** Moisten a small quantity of the solid substance on a watch-glass or in a small dish with concentrated hydrochloric acid. On dipping the tip of a platinum wire into the mixture a small

quantity will adhere. Introduce at the base of the flame, and note the colour produced.

Bright green or blue flame indicates **Copper**.

Light green (apple-green) flame indicates **Barium**.

Brick-red flame indicates **Calcium**.

(Crimson flame indicates **Strontium** or **Lithium**.)

Violet flame indicates **Potassium**.

Intense yellow flame indicates **Sodium**.

NOTES.—(1) A **Blue flame**, which must not be confused with the violet potassium flame, is given by **Lead**, **Bismuth**, **Arsenic**, and **Antimony**. These substances **corrode the platinum wire**, so that if they are suspected one is very careful in carrying out the platinum wire test, and should desist at once on noticing the blue flame, otherwise the end of the platinum wire is rendered brittle and breaks off.

(2) The wire should be cleaned between each test. To effect this, dip the wire repeatedly into concentrated hydrochloric acid, and then into the flame until no tint is given. Barium is particularly difficult to remove completely from a wire, especially if the heating with the barium salt has been prolonged.

(3) In order to clean the wire thoroughly after each day's work it is a good plan to have the free end of the glass rod fixed into a cork, which fits a test-tube containing a few c.c. of concentrated hydrochloric acid. The position of the wire should be so adjusted that on corking the test-tube, the end of the wire dips into the acid.



## B. WET TESTS FOR THE METALS.

**Preliminary Note.**—The wet tests for the metals generally depend upon the precipitation of compounds, often of characteristic appearance, under definite conditions.

The student should understand at the outset that the reason for the formation of the numerous precipitates is simply that the bodies thrown down can be formed under the conditions of the experiment, and being insoluble under these circumstances are precipitated. He should recognize that if the conditions were altered, e. g. if in a particular case the solution was rendered strongly acid or alkaline before addition of the reagent, no precipitate might form.

It is very important also that he should grasp the fact that the List of Reactions given under each metal affords information regarding many of the chief compounds of the metal, and is therefore important from both practical and theoretical points of view. Indeed, a thorough knowledge of the reactions detailed below and the reasons for precipitation in each case should help a student greatly with his theoretical work.

In carrying out wet tests for identification of metals, they are conveniently divided into six groups, depending upon their behaviour towards certain compounds called **Group Reagents**.

**Group I. Silver group:** includes Ag, Hg<sup>ous</sup>, Pb.

„ **II.** { **II a. Copper group:** includes Cu, Bi, Hg<sup>ic</sup>, (Pb).  
 { **II b. Arsenic Subgroup:** includes As, Sb, Sn<sup>ous</sup>, Sn<sup>ic</sup>.

„ **III. Aluminium Group:** includes Al, Cr, Fe<sup>ous</sup>, Fe<sup>ic</sup>.

„ **IV. Zinc group:** includes Zn, Mn.

„ **V. Calcium group:** includes Ba, Sr, Ca.

„ **VI. This is a heterogeneous group:** Mg, NH<sub>4</sub>, K, Na.

The reason for the above arrangement into groups will be fully considered on p. 141, after the reactions of the metals have been summarized. In carrying out the following reactions a student should take 1–2 c.c. of solution of the given metallic salt in a test-tube, and add a few drops of the reagent. If a precipitate occurs, he should try to write the equation expressing the reaction, so as to make certain that he comprehends exactly what has taken place.

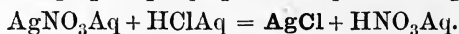
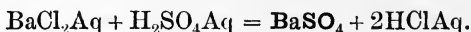
If not sufficiently advanced to do so satisfactorily, he should study the equation given in the book. During analysis it is most important that equations should be written, and the valency table (p. 5) should be consulted for first attempts.

The following general points should be noted in connexion with Precipitation Reactions:—

(1) **Temperature** affects the result in most cases by accelerating the rate of interaction; therefore warming the reaction mixture may produce a precipitate, which might form so slowly in a cold dilute solution that it would be liable to escape observation.

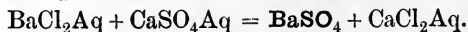
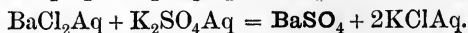
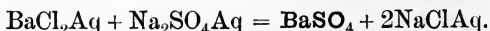
(2) Reactions generally take place by **Double Decomposition** between two of the substances in solution. A chance is given for an insoluble compound to form, and it comes down: for example, if we add sulphuric acid to a solution of barium chloride a precipitate of barium sulphate forms, and if hydrochloric acid is added to a solution of silver nitrate a precipitate of silver chloride comes down.

Equations:

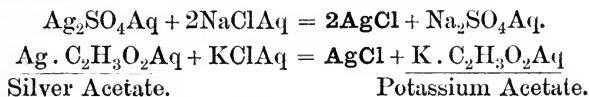


(3) Note that what really conditions the formation of any particular precipitate is the presence of certain radicles or ions, e.g. (a) In the precipitation of barium sulphate from a solution, the ions barium (Ba) and sulphion ( $\text{SO}_4$ ) must be present. In using this reaction as a confirmatory test for the metal barium, dilute sulphuric acid is usually the reagent added which contains the sulphion ion. The student should note, however, that any salt in solution containing the sulphion radicle would cause a similar reaction; e.g. sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), sodium hydrogen sulphate ( $\text{NaHSO}_4$ ), potassium sulphate ( $\text{K}_2\text{SO}_4$ ), ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ), copper sulphate ( $\text{CuSO}_4$ ), aluminium sulphate ( $\text{Al}_2(\text{SO}_4)_3$ ), ferrous sulphate ( $\text{FeSO}_4$ ), calcium sulphate ( $\text{CaSO}_4$ ), and magnesium sulphate ( $\text{MgSO}_4$ ) would all cause precipitation of barium sulphate if added to a solution of a barium salt; e.g.

Equations:



(b) The precipitation of silver chloride is generally effected by adding dilute hydrochloric acid to a solution of a silver salt, the ions which must be present being silver (Ag) and chlorine (Cl). Silver ions are present in a solution of any silver salt, and chlorine ions in any solution of a chloride, so that any soluble silver salt added to any soluble chloride will cause the precipitation of silver chloride; e. g.



(4) Note the interchangeability of reagent and reacting body. Take above cases for example.

(a) Any soluble sulphate produces a precipitate of barium sulphate ( $\text{BaSO}_4$ ) with a solution of a barium salt, and therefore the addition of any soluble sulphate to a solution would constitute a test for barium, and, conversely, the addition of any soluble barium salt to a solution would constitute a test for a sulphate.

(b) Any soluble chloride causes the precipitation of silver chloride on addition to a soluble silver salt, and therefore the addition of a soluble chloride (e. g. hydrogen chloride, hydrochloric acid) constitutes a test for a silver salt, and, conversely, the addition of a silver salt constitutes a test for a soluble chloride.

(5) Many substances may prevent precipitation of a compound insoluble in water even if the required ions should be present in pure aqueous solution; e. g. concentrated acids and alkalis will often entirely prevent reactions from taking place. As the student must effect the solution of many substances in acids, he should therefore use a minimum of acid, otherwise many reactions may be prevented or modified.

Note carefully the necessary precautions in the following lists of reactions. In order to make the summary as convenient for reference as possible, the dry tests are added at the end of each list. Certain negative tests are given in some cases as facts which a student should know and as bearing on the general scheme of analysis.

In order to gain space, only the formulae for the reagents used are given, and in order to prevent chance of mistake the following is a complete list of the reagents generally employed. The arrangement followed is that used at the Examination Hall of the Royal Colleges of Physicians and Surgeons.

**Lists of Compounds of the Metals.**

The Summary of Important Compounds of each Metal which follows the List of Tests will, it is hoped, help a student to correlate his practical and theoretical work. After identification of a simple substance or of the constituents of a mixture, the candidate should consult the Lists and consider whether the properties agree with those indicated by experiment.

The numbers given in the last column of the Summary bear reference to the general methods of preparing salts previously detailed, viz.:—

1. Action of Acid upon a Metallic Oxide or Hydroxide (i. e. acid upon base).
2. Action of Acid upon the Carbonate of a Metal (p. 53).
3. Action of Acid upon a Metal (p. 54).
4. Precipitation (p. 55). This method can be used for preparation of many other compounds besides salts; e. g. many hydroxides can be obtained in this way.

## LIST OF REAGENTS.

Name.	Formula.	Name.	Formula.
Acetic Acid dil.	$\left\{ \begin{array}{l} \text{CH}_3\text{COOH} \\ \text{or } \text{H}_2\text{C}_2\text{H}_3\text{O}_2 \end{array} \right.$	(Potassium Dichromate)	$\text{K}_2\text{Cr}_2\text{O}_7$
Hydrochloric Acid dil.	$\text{HCl}$	Potassium Ferricyanide	$\text{K}_3\text{Fe}(\text{CN})_6$
Nitric Acid dil.	$\text{HNO}_3$	Potassium Ferrocyanide	$\text{K}_4\text{Fe}(\text{CN})_6$
Sulphuric Acid dil.	$\text{H}_2\text{SO}_4$	Potassium Iodide	$\text{KI}$
Tartaric Acid	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	Potassium Sulphate	$\text{K}_2\text{SO}_4$
Sulphuretted Hydrogen or Hydrogen Sulphide	$\text{SH}_2$	Stannous Chloride	$\text{SnCl}_2$
Ammonium Hydroxide	$\text{NH}_4\text{OH}$	Borax, solid	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Calcium Hydroxide or Lime-water	$\text{Ca}(\text{OH})_2$	Copper turnings and foil	$\text{Cu}$
Potassium Hydroxide	$\text{KOH}$	Ferrous Sulphate, solid	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Ammonium Carbonate	$(\text{NH}_4)_2\text{CO}_3$	Manganese Dioxide, solid	$\text{MnO}_2$
Ammonium Chloride	$\text{NH}_4\text{Cl}$	Microcosmic Salt, solid	$\text{H.Na.NH}_4\text{PO}_4 \cdot 4\text{H}_2\text{O}$
Ammonium Oxalate	$(\text{NH}_4)_2\text{C}_2\text{O}_4$	Potassium Nitrate, solid	$\text{KNO}_3$
Ammonium Sulphide	$(\text{NH}_4)_2\text{S}$	Sodium Carbonate, solid anhydrous	$\text{Na}_2\text{CO}_3$
Barium Nitrate	$\text{Ba}(\text{NO}_3)_2$	Starch, solid	$(\text{C}_6\text{H}_{10}\text{O}_5)_x$
Calcium Chloride	$\text{CaCl}_2$	Test Papers:—Litmus red, Litmus blue, Turmeric	
Calcium Sulphate	$\text{CaSO}_4$	Zinc, solid	$\text{Zn}$
Chlorine Water	$\text{Cl}_2\text{Aq}$	Ethyl Alcohol	$\text{C}_2\text{H}_5\text{OH}$
Magnesium Sulphate	$\text{MgSO}_4$	Ammonium Molybdate (generally with Nitric Acid present)	$(\text{NH}_4)_2\text{MoO}_4$
Sodium Carbonate	$\text{Na}_2\text{CO}_3$	Chloroform	$\text{CHCl}_3$
Sodium Phosphate	$\text{Na}_2\text{HPO}_4$	Barium Chloride	$\text{BaCl}_2$
Hydrochloric Acid Conc.	$\text{HCl}$	Cobalt Nitrate (Indigo)	$\text{Co}(\text{NO}_3)_2$
Nitric Acid Conc.	$\text{HNO}_3$	Iodine in Potassium Iodide	$\text{I}_2$
Sulphuric Acid Conc.	$\text{H}_2\text{SO}_4$	Platinic Chloride	$\left\{ \begin{array}{l} \text{H}_2\text{PtCl}_6 \\ \text{AgNO}_3 \end{array} \right.$
Ammonium Sulphocyanide	$\text{NH}_4\text{SCN}$	Hydrochloroplatinic Acid	
Copper Sulphate	$\text{CuSO}_4$	Silver Nitrate	$\text{AgNO}_3$
Ferric Chloride	$\text{FeCl}_3$	Starch Paste	$(\text{C}_6\text{H}_{10}\text{O}_5)_x$
Ferrous Sulphate	$\text{FeSO}_4$	Sodium Hypobromite	$\text{NaOBr}$
Lead Acetate	$\left\{ \begin{array}{l} \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \\ \text{or} \\ (\text{CH}_3\text{COO})_2\text{Pb} \end{array} \right.$		
Mercuric Chloride	$\text{HgCl}_2$		
Mercurous Nitrate	$\text{HgNO}_3$		
Potassium Chromate	$\text{K}_2\text{CrO}_4$		

## Summary of Tests for the Metals.

GENERAL DIRECTIONS FOR WET TESTS:—Add a few drops of reagent to about 2 c.c. of solution of substance and warm gently if necessary.

## Group I. Silver. Mercurous Salts. Lead.

## Summary of Reactions. Silver. Ag. 108.

A solution of Silver Nitrate can be used in carrying out the wet tests.

Reagent.	Results observed.	Remarks.
1. HCl	White curdy precipitate of Silver Chloride, insoluble in water and Nitric Acid, but readily soluble in $\text{NH}_4\text{OH}$ aq. e. g. $\text{AgNO}_3\text{Aq} + \text{HClAq} = \text{AgCl} + \text{HNO}_3\text{Aq}$ Silver Nitrate                      Silver Chloride	Acids may be present.
2. $\text{H}_2\text{S}$	Black precipitate of Silver Sulphide, soluble in boiling dil. $\text{HNO}_3$ . $2\text{AgNO}_3\text{Aq} + \text{H}_2\text{S} = \text{Ag}_2\text{S} + 2\text{HNO}_3\text{Aq}$ Silver Nitrate                      Silver Sulphide	Free Nitric Acid should not be present in large quantity.
3. $(\text{NH}_4)_2\text{S}$	Black precipitate of Silver Sulphide. $2\text{AgNO}_3\text{Aq} + (\text{NH}_4)_2\text{SAq} = \text{Ag}_2\text{S} + 2\text{NH}_4\text{NO}_3\text{Aq}$ Ammon. Sulphide                      Ammon. Nitrate	
4. $\text{K}_2\text{CrO}_4$	Reddish precipitate of Silver Chromate, soluble in acids. $2\text{AgNO}_3\text{Aq} + \text{K}_2\text{CrO}_4\text{Aq} = \text{Ag}_2\text{CrO}_4 + 2\text{KNO}_3\text{Aq}$ Potassium Chromate                      Silver Chromate	Free acids should not be present.
5. KI	Faintly yellow precipitate of Silver Iodide. $\text{AgNO}_3\text{Aq} + \text{KIAq} = \text{AgI} + \text{KNO}_3\text{Aq}$ Potassium Iodide                      Silver Iodide	
6. KOH or NaOH	Greyish precipitate of Silver Oxide. $2\text{AgNO}_3\text{Aq} + 2\text{KOH aq} = \text{Ag}_2\text{O} + 2\text{KNO}_3\text{Aq} + \text{H}_2\text{O}$ Silver Oxide	Free acids should not be present.
7. $\text{NH}_4\text{OH}$	Greyish precipitate of Silver Oxide, readily soluble in excess. $\text{AgNO}_3\text{Aq} + 2\text{NH}_4\text{OH aq} = \text{Ag}_2\text{O} + 2\text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$	Very dilute Ammonium Hydroxide solution should be used. Add a few drops of solution on bench to about 20 c.c. water.
8. Charcoal	Heated on Charcoal with fusion mixture a brilliant silvery bead is obtained. (The bead readily dissolves in Nitric Acid, and the solution would give above tests.)	

**Summary regarding Silver and its notable Compounds,**  
most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
<b>Ag</b>	<b>Metallic Silver</b>	Brilliant lustre. Met with as foil, powder, &c.	Soluble in $\text{HNO}_3$ . Insol. in $\text{HCl}$ and dil. $\text{H}_2\text{SO}_4$ .	Reduction processes.
<b><math>\text{AgNO}_3</math></b>	<b>Silver Nitrate</b>	White cryst. solid. Slowly affected by light.	Soluble in water.	1. 2. 3
<b>(<math>\text{AgNO}_2</math></b>	<b>Silver Nitrite</b>	Nearly white solid.	Slightly soluble in water.)	4
<b><math>\text{AgCl}</math></b>	<b>Silver Chloride</b>	White solid. Rapidly affected by light.	Insol. in water and acids. Readily soluble in $\text{NH}_4\text{OH}$ aq.	4
<b><math>\text{AgBr}</math></b>	<b>Silver Bromide</b>	Very faint yellow compound.	Insol. in water and acids. Sol. in $\text{NH}_4\text{OH}$ aq. with difficulty.	4
<b><math>\text{AgI}</math></b>	<b>Silver Iodide</b>	Light yellow solid.	Insol. in water, acids, and $\text{NH}_4\text{OH}$ aq.	4
<b><math>\text{Ag}_2\text{CO}_3</math></b>	<b>Silver Carbonate</b>	White solid.	Insol. in water. Soluble in many acids with decomposition.	4
<b><math>\text{Ag}_2\text{SO}_4</math></b>	<b>Silver Sulphate</b>	White cryst. solid.	Sparingly soluble in water.	1. 2. (3)
<b>(<math>\text{Ag}_2\text{SO}_3</math></b>	<b>Silver Sulphite</b>	White solid.	Insol. in water. Soluble in acids with decomposition.)	4
<b><math>\text{Ag}_3\text{PO}_4</math></b>	<b>Silver Phosphate</b>	Light yellow solid.	Insol. in water. Soluble in $\text{HNO}_3$ and in $\text{NH}_4\text{OH}$ .	4
<b><math>\text{Ag}_3\text{AsO}_3</math></b>	<b>Silver Arsenite</b>	do. do.	do. do.	4
<b><math>\text{Ag}_3\text{AsO}_4</math></b>	<b>Silver Arsenate</b>	Reddish brown solid.	do. do.	4
<b><math>\text{Ag}_2\text{CrO}_4</math></b>	<b>Silver Chromate</b>	Dark red solid.	Insol. in water. Soluble in $\text{HNO}_3$ to give a yellow solution.	4
<b><math>\text{Ag}_2\text{Cr}_2\text{O}_7</math></b>	<b>Silver Dichromate</b>	do. do.		
<b><math>\text{AgCN}</math></b>	<b>Silver Cyanide</b>	White solid.	Insol. in water, but sol. in $\text{NH}_4\text{OH}$ aq., $\text{KCNA}$ aq., and (with difficulty) in conc. $\text{HNO}_3$ .	4
<b><math>\text{Ag}_2\text{S}</math></b>	<b>Silver Sulphide</b>	Black solid.	Insol. in water. Sol. in boiling $\text{HNO}_3$ .	4
<b><math>\text{Ag}_2\text{O}</math></b>	<b>Silver Oxide</b>	Grey or black solid.	Insol. in water. Sol. in $\text{HNO}_3$ and in $\text{NH}_4\text{OH}$ aq.	4

Alloy :—British Coinage, 92.5 % Ag : 7.5 % Cu.

# Summary of Reactions. Mercurous Mercury. $\text{Hg}^{\text{ous}}$ or $\text{Hg}^{\cdot}$ .

Use a solution of Mercurous Nitrate.

Reagent.	Results observed.	Remarks.
1. $\text{HCl}$	<p><b>White precipitate of Mercurous Chloride.</b>  <math>\text{HgNO}_3\text{Aq} + \text{HClAq} = \text{HgCl} + \text{HNO}_3\text{Aq}</math>            Mercurous Nitrate                      Mercurous Chloride            On pouring off the supernatant liquid and adding Ammonia Solution the precipitate turns black.  <math>2\text{HgCl} + 2\text{NH}_3\text{Aq} = \text{NH}_2\text{Hg}_2\text{Cl} + \text{NH}_4\text{ClAq}</math>            Mercurous Chloride                      Dimereurous Ammonium Chloride</p>	Distinction from Mercuric Compounds.
2. $\text{H}_2\text{S}$	A black precipitate which chiefly consists of <b>Mercuric Sulphide and Mercury</b> is obtained. e.g. $2\text{HgNO}_3\text{Aq} + \text{H}_2\text{S} = \text{HgS} + \text{Hg} + 2\text{HNO}_3\text{Aq}$	Mercuric Compounds give a similar precipitate of Mercuric Sulphide ( $\text{HgS}$ ).
3. $(\text{NH}_4)_2\text{S}$	A black precipitate which may consist chiefly of <b>Mercurous Sulphide</b> comes down. $2\text{HgNO}_3\text{Aq} + (\text{NH}_4)_2\text{SAq} = \text{Hg}_2\text{S} + 2\text{NH}_4\text{NO}_3$	do.                      do.
4. $\text{KOH}$ or $\text{NaOH}$	<p><b>Black precipitate of Mercurous Oxide</b> forms.  <math>2\text{HgNO}_3\text{Aq} + 2\text{KOH Aq} = \text{Hg}_2\text{O} + \text{H}_2\text{O} + 2\text{KNO}_3\text{Aq}</math>            Potassium Hydroxide                      Potassium Nitrate</p>	Distinction from Mercuric Compounds (cf. p. 102).
5. $\text{KI}$	<p><b>Finch green precipitate of Mercurous Iodide</b>, soluble in excess of Potassium Iodide.  <math>\text{HgNO}_3\text{Aq} + \text{KIAq} = \text{HgI} + \text{KNO}_3\text{Aq}</math>            Mercurous Iodide</p>	Distinction from Mercuric Compounds (cf. p. 102).
6. $\text{SnCl}_2$	<p>First a <b>white precipitate of Mercurous Chloride</b> comes down, and then with excess of reagent on warming a <b>grey precipitate of Metallic Mercury</b> appears.            a) <math>2\text{HgNO}_3\text{Aq} + \text{SnCl}_2\text{Aq} = 2\text{HgCl} + \text{SnCl}_4\text{Aq}</math>                                                     Stannous Mercurous Stannic Chloride Chloride Chloride            b) <math>2\text{HgCl} + \text{SnCl}_2\text{Aq} = 2\text{Hg} + \text{SnCl}_4\text{Aq}</math></p>	The second part of this reaction is given by Mercuric Compounds.
7. $\text{Cu}$ and $\text{HCl}$	A strip of Metallic Copper warmed gently with a solution of a mercury salt acidified by $\text{HCl}$ has a <b>coating of Mercury</b> deposited upon it. On removing the strip after warming for a few minutes, and rubbing between filter paper, the silvery appearance is very characteristic.	Mercuric Compounds react similarly.
8. $\text{K}_2\text{CrO}_4$	<p>Light red precipitate of Mercurous Chromate.  <math>2\text{HgNO}_3\text{Aq} + \text{K}_2\text{CrO}_4\text{Aq} = \text{Hg}_2\text{CrO}_4 + 2\text{KNO}_3\text{Aq}</math></p>	
9. Carbon and $\text{Na}_2\text{CO}_3$	On heating in a bulb tube dry substance mixed with $\text{C}$ and $\text{Na}_2\text{CO}_3$ , a <b>sublimate of Mercury</b> is obtained.	Mercuric Compounds behave in similar way.



**Summary regarding Mercury and Mercurous Compounds,**

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
Hg	<b>Metallic Mercury</b>	Silvery liquid.	Insoluble in water, soluble in Nitric Acid. Insol. in HCl and dil. Sulphuric Acid. (Sol. in conc. Sulphuric Acid.)	
HgNO <sub>3</sub>	<b>Mercurous Nitrate</b>	Nearly white solid.	Soluble in water. Basic yellowish insoluble salts may be met with.	3
HgCl	<b>Mercurous Chloride</b> (Calomel)	White solid.	Insoluble in water. Blackened by NH <sub>4</sub> OH. Dissolved by aqua regia (HCl and HNO <sub>3</sub> ).	4 or heat mixture of Hg <sub>2</sub> SO <sub>4</sub> and NaCl.
HgBr	<b>Mercurous Bromide</b>	White solid.	Insoluble in water. Soluble in aqua regia.	4
HgI (or Hg <sub>2</sub> I <sub>2</sub> )	<b>Mercurous Iodide</b>	Finch green solid.	Insol. in water. Soluble in KIAq and in aqua regia.	4
Hg <sub>2</sub> SO <sub>4</sub>	<b>Mercurous Sulphate</b>	White solid.	Slightly soluble in water.	3
Hg <sub>2</sub> O	<b>Mercurous Oxide</b>	Black solid.	Insol. in water. Soluble in Nitric Acid.	4
Hg. C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	<b>Mercurous Acetate</b>	White solid.	Soluble in water.	1

Alloys of Metals with Mercury are termed Amalgams.

## Summary of Reactions. Lead. At. wt. 207.

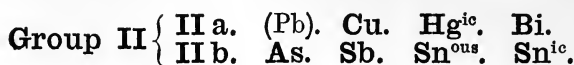
Use a solution of Lead Acetate or Lead Nitrate in carrying out the wet tests.

Reagent.	Results observed.	Remarks.
1. HCl	<p>White precipitate of Lead Chloride, insoluble in <math>\text{NH}_4\text{OHAq}</math>.</p> <p>e. g. <math>\text{Pb}(\text{NO}_3)_2\text{Aq} + 2\text{HClAq} = \text{PbCl}_2 + 2\text{HNO}_3\text{Aq}</math></p> <p style="text-align: center;">Lead Chloride</p> <p><math>(\text{CH}_3\text{COO})_2\text{PbAq} + 2\text{HClAq}</math></p> <p style="text-align: center;">Lead Acetate</p> <p style="text-align: center;"><math>= \text{PbCl}_2 + 2\text{CH}_3\cdot\text{COOHAq}</math></p> <p style="text-align: center;">Acetic Acid</p> <p>The precipitate is soluble on boiling with a moderate quantity of water, and separates in characteristic white crystals on cooling.</p>	The solution should not be very dilute, otherwise no precipitate may form, as Lead Chloride is <i>slightly</i> soluble in water. A large quantity of concentrated Hydrochloric Acid should not be present.
2. $\text{H}_2\text{S}$	<p>Black precipitate of Lead Sulphide forms.</p> <p>e. g. <math>\text{Pb}(\text{NO}_3)_2\text{Aq} + \text{H}_2\text{S} = \text{PbS} + 2\text{HNO}_3\text{Aq}</math></p>	Free acids should not be present in large quantity. With a fairly large amount of Hydrochloric Acid present a reddish precipitate of $\text{PbS}$ . $\text{PbCl}_2$ is first precipitated.
3. $(\text{NH}_4)_2\text{S}$	<p>Black precipitate of Lead Sulphide.</p> <p><math>\text{Pb}(\text{NO}_3)_2\text{Aq} + (\text{NH}_4)_2\text{SAq} = \text{PbS} + 2\text{NH}_4\text{NO}_3\text{Aq}</math></p>	Free acids should not be present.
4. $\text{K}_2\text{CrO}_4$	<p>Yellow precipitate of Lead Chromate.</p> <p>e. g. <math>(\text{CH}_3\cdot\text{COO})_2\text{Pb} + \text{K}_2\text{CrO}_4\text{Aq}</math></p> <p style="text-align: center;">Lead Acetate      Potassium Chromate</p> <p style="text-align: center;"><math>= \text{PbCrO}_4 + 2\text{CH}_3\text{COOKAq}</math></p> <p style="text-align: center;">Lead Chromate      Potassium Acetate</p>	Free acids should not be present in large quantity.
5. KI	<p>Yellow precipitate of Lead Iodide (<math>\text{PbI}_2</math>).</p> <p>On pouring off the supernatant liquid and boiling the precipitate with water, the Lead Iodide dissolves and crystallizes on cooling in characteristic golden spangles.</p> <p>e. g. <math>\text{Pb}(\text{NO}_3)_2\text{Aq} + 2\text{KIAq} = \text{PbI}_2 + 2\text{KNO}_3\text{Aq}</math></p> <p><math>(\text{CH}_3\cdot\text{COO})_2\text{PbAq} + 2\text{KIAq} = \text{PbI}_2 + 2\text{CH}_3\text{COOKAq}</math></p> <p style="text-align: center;">Pot. Iodide      Lead Iodide</p>	Certain free acids, e. g. Nitric Acid, should not be present.
6. $\text{H}_2\text{SO}_4$	<p>Heavy white precipitate of Lead Sulphate.</p> <p>e. g. <math>\text{Pb}(\text{NO}_3)_2\text{Aq} + \text{H}_2\text{SO}_4\text{Aq} = \text{PbSO}_4 + 2\text{HNO}_3\text{Aq}</math></p>	
7. KOH, NaOH, or $\text{NH}_4\text{OH}$	<p>White precipitate of Lead Hydroxide.</p> <p>e. g. <math>\text{Pb}(\text{NO}_3)_2\text{Aq} + 2\text{KOHAcq} = \text{Pb}(\text{OH})_2 + 2\text{KNO}_3\text{Aq}</math></p> <p style="text-align: center;">Potassium Hydroxide      Lead Hydroxide</p>	
8. C	<p>Heated on Charcoal with or without fusion mixture, a characteristic malleable bead which marks paper is obtained.</p> <p>e. g. on heating Lead Nitrate it first splits up to give Lead Oxide, which readily reduces.</p> <p>a) <math>2\text{Pb}(\text{NO}_3)_2 = 2\text{PbO} + 4\text{NO}_2 + \text{O}_2</math></p> <p>b) <math>\text{PbO} + \text{C} = \text{Pb} + \text{CO} \rightarrow</math></p>	
9. Flame test	On Platinum Wire a blue flame is obtained.	The Platinum wire is so rapidly corroded that it is not advisable to use this test.

# Summary regarding Lead and Lead Compounds, most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
Pb	Metallic Lead	Bluishwhite metal. Met with in many forms, e.g. sheet, granulated, foil, wire, &c.	Slightly affected by pure water with formation of Hydroxide. Dissolves in Nitric and Acetic Acids. HCl and dil. H <sub>2</sub> SO <sub>4</sub> hardly attack it.	Reduction on Carbon, &c.
Pb(NO <sub>3</sub> ) <sub>2</sub>	Lead Nitrate	White cryst. solid. Decomposes on heating, giving brown fumes of NO <sub>2</sub> .	Soluble in water.	1. 2. 3
PbCl <sub>2</sub>	Lead Chloride	White cryst. solid.	Slightly soluble in cold water; more soluble in hot water and in concentrated Hydrochloric Acid.	4
(PbBr <sub>2</sub> )	Lead Bromide	White cryst. solid.	do. do.	4)
PbI <sub>2</sub>	Lead Iodide	Yellow cryst. solid. May be met with as characteristic golden spangles.	Slightly sol. in cold water; moderately soluble in boiling water, from which it can be recrystallized as golden spangles.	4
PbCO <sub>3</sub>	Lead Carbonate	White solid (occurs native as Cerussite). White Lead is a basic Lead Carbonate.	Soluble in Nitric and Acetic Acids.	4
PbSO <sub>4</sub>	Lead Sulphate	White solid.	Nearly insol. in water. Sol. in Potassium Hydroxide and Ammonium Acetate.	4
Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Lead Phosphate	White solid.	Insoluble in water. Soluble in Nitric Acid.	4
PbCrO <sub>4</sub>	Lead Chromate	Yellow solid.	Insol. in water. Soluble in Nitric Acid unless after ignition, when it becomes very insoluble.	4
Pb.(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> .3H <sub>2</sub> O or (CH <sub>3</sub> .COO) <sub>2</sub> Pb.3H <sub>2</sub> O	Lead Acetate (Sugar of Lead)	White crystalline solid, sweet taste.	Soluble in water.	1. 2. 3
PbC <sub>2</sub> O <sub>4</sub>	Lead Oxalate	White solid.	Insoluble in water. Soluble in Nitric Acid.	4
PbS	Lead Sulphide (ore is termed Galena)	Met with as a black powder or substance with metallic lustre (Galena).	Dissolves in moderately concentrated Nitric Acid, with partial conversion into PbSO <sub>4</sub> . Insoluble in water.	4
Pb(OH) <sub>2</sub>	Lead Hydroxide	White solid.	Soluble in Nitric Acid or Acetic Acid.	4
PbO	Lead Oxide	Met with in allotropic modifications: Orange compound — <b>Litharge</b> ; Light yellow compound — <b>Massicot</b> .	Nearly insol. in water. Soluble with difficulty in boiling HCl, but readily soluble in Nitric or in Acetic Acid.	Heat metal in oxidizing blast.
Pb <sub>3</sub> O <sub>4</sub>	Red Lead (Triplumbic Tetroxide)	Bright red heavy solid. Turns yellow on heating strongly, oxygen being evolved.	Soluble in conc. HCl with evolution of Chlorine. Pb <sub>3</sub> O <sub>4</sub> + 8HCl = 3PbCl <sub>2</sub> + 4H <sub>2</sub> O + Cl <sub>2</sub> With Nitric Acid turns brown from separation of Lead Peroxide. Pb <sub>3</sub> O <sub>4</sub> + 4HNO <sub>3</sub> Aq = PbO <sub>2</sub> + 2Pb(NO <sub>3</sub> ) <sub>2</sub> Aq + 2H <sub>2</sub> O	Heat PbO to 400° C. in air.
PbO <sub>2</sub>	Lead Peroxide	Deep brown powder.	Soluble in conc. HCl with separation of white crystals of Lead Chloride and evolution of Chlorine. PbO <sub>2</sub> + 4HClAq = PbCl <sub>2</sub> + 2H <sub>2</sub> O + Cl <sub>2</sub> ↗	Action of HNO <sub>3</sub> on Pb <sub>3</sub> O <sub>4</sub> , &c.

Alloys:—Type Metal, 75 % Pb : 20 % Sb : 5 % Sn. Shot, Pb. As. Soft Solder, 0 % Pb : 50 % Sn. Pewter, 25 % Pb : 75 % Sn.



### Summary of Reactions. Copper. Cu. At. wt. 63.

Use a solution of Copper Sulphate or Chloride for wet tests.

Reagent.	Results observed.	Remarks.
<b>Note.</b> Solutions of Copper Compounds are generally blue or green.		
1. HCl	No reaction.	
2. H <sub>2</sub> S	<b>Black precipitate of Copper Sulphide.</b> e. g. $\text{CuSO}_4\text{Aq} + \text{H}_2\text{S} = \text{CuS} + \text{H}_2\text{SO}_4\text{Aq}$ <div style="display: flex; justify-content: space-around; width: 100%;"> <span>Copper Sulphate</span> <span>Copper Sulphide</span> </div>	
3. (NH <sub>4</sub> ) <sub>2</sub> S	<b>Black precipitate of Copper Sulphide.</b> $\text{CuSO}_4\text{Aq} + (\text{NH}_4)_2\text{S} = \text{CuS} + (\text{NH}_4)_2\text{SO}_4\text{Aq}$ <div style="display: flex; justify-content: space-around; width: 100%;"> <span>Ammon. Sulphate</span> </div>	
4. KOH or NaOH	<b>Blue precipitate of Cupric Hydroxide</b> forms from a cold solution. $\text{CuSO}_4\text{Aq} + 2\text{NaOHAq} = \text{Cu}(\text{OH})_2 + \text{Na}_2\text{SO}_4\text{Aq}$ <div style="display: flex; justify-content: space-around; width: 100%;"> <span>Copper Hydroxide</span> </div> <p>On boiling with excess of alkaline Hydroxide the precipitate turns black, owing to partial dehydration to Cupric Oxide.  <math>\text{Cu}(\text{OH})_2 + \text{CuO} + \text{H}_2\text{O}</math></p>	
5. NH <sub>4</sub> OH	<b>Blue precipitate of Copper Hydroxide</b> , readily soluble in excess of reagent, giving a deep blue solution. e. g. $\text{CuSO}_4\text{Aq} + 2\text{NH}_4\text{OHAq} = \text{Cu}(\text{OH})_2 + (\text{NH}_4)_2\text{SO}_4\text{Aq}$	
6. K <sub>4</sub> Fe(CN) <sub>6</sub>	<b>Brown precipitate of Copper Ferrocyanide.</b> $2\text{CuSO}_4\text{Aq} + \text{K}_4\text{Fe}(\text{CN})_6\text{Aq} = \text{Cu}_2\text{Fe}(\text{CN})_6 + 2\text{K}_2\text{SO}_4\text{Aq}$	Much free acid should not be present.
7. KI	<b>White precipitate of Cuprous Iodide</b> with simultaneous liberation of Iodine, which colours the solution brown. $2\text{CuSO}_4\text{Aq} + 4\text{KIAq} = \text{Cu}_2\text{I}_2 + \text{I}_2 + 2\text{K}_2\text{SO}_4\text{Aq}$	Note.—Most Copper Compounds are Cupric Compounds.
8. Fe or Zn	<b>Copper</b> is precipitated by replacement. $\text{CuSO}_4\text{Aq} + \text{Fe} = \text{Cu} + \text{FeSO}_4\text{Aq}$ $\text{CuSO}_4\text{Aq} + \text{Zn} = \text{Cu} + \text{ZnSO}_4\text{Aq}$	The metals Zn and Fe are more oxidizable than Copper, and as a rule a more oxidizable metal replaces a less oxidizable in solution.
9. Platinum wire test	<b>Green and blue flame.</b>	Moisten the substance with concentrated Hydrochloric Acid before testing.
10. Borax bead test	<b>Blue bead.</b>	
11. C	Heated on Carbon with fusion mixture (and KCN) <b>reddish scales of metallic Copper</b> are obtained with difficulty.	

## Summary regarding Copper and Copper Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
Cu	<b>Metallic Copper</b>	Reddish metal. Met with as foil, wire, turnings, &c.	Insoluble in water, HCl, and dil. $H_2SO_4$ . Readily soluble in Nitric Acid. Reacts with conc. $H_2SO_4$ .	Reduction on Carbon, &c.
<b>A. CUPRIC COMPOUNDS :—</b>				
$Cu(NO_3)_2$	<b>Copper Nitrate</b>	Blue solid. Decomposes on heating, giving brown fumes of $NO_2$ . $2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$	Soluble in water.	1. 2. 3
$CuCl_2$	<b>Cupric Chloride</b>	Hydrated Compound is generally green. (Anhydrous substance is brown.)	Soluble in water to give a green (or blue) solution.	1. 2
$CuBr_2$	<b>Cupric Bromide</b>	Unknown.)	Soluble in water.	1. 2
$(CuI_2)$	<b>Cupric Iodide</b>			
$CuCO_3$	<b>Copper Carbonate</b> (Basic Compounds are generally met with).	Blue powder. A natural basic Carbonate, Malachite, $2CuCO_3 \cdot Cu(OH)_2$ , is green. Azurite, another ore, is blue, $CuCO_3 \cdot Cu(OH)_2$ .	Insoluble in water. Soluble in acids.	4
$CuSO_4 \cdot 5H_2O$	<b>Copper Sulphate</b>	Blue crystalline solid. On heating to $210^\circ C$ . a white powder, $CuSO_4$ , can be obtained.	Soluble in water.	1. 2. (3)
$Cu_3(PO_4)_2$	<b>Copper Phosphate</b>	Blue powder.	Insoluble in water. Soluble in acids.	4
$Cu(C_2H_3O_2)_2$	<b>Copper Acetate</b>	Blue cryst. solid.	Soluble in water.	1. 2
$CuS$	<b>Copper Sulphide</b>	Black powder.	Insol. in water. Soluble in boiling dilute Nitric Acid.	4
$CuO$	<b>Cupric Oxide</b>	Black solid. Met with as powder or in granular form.	Insoluble in water. Soluble in acids.	Heat nitrate or 4.
<b>B. CUPROUS COMPOUNDS :—</b>				
$Cu_2Cl_2$	<b>Cuprous Chloride</b>	White solid.	Insoluble in water. Soluble in conc. HCl and in $NH_4OH$ .	4
$Cu_2I_2$	<b>Cuprous Iodide</b>	do.	Insoluble in water.	
$Cu_2O$	<b>Cuprous Oxide</b>	Red powder.	do.	4

Alloys:—Brass, 60–80 % Cu : 40–20 % Zn.  
Bronze, Cu, Zn, Sn, Pb.

German Silver, Cu, Zn, Ni.  
Gun and Bell Metal, Cu, Sn.

Summary of Reactions of } Mercury in Mercuric state.  
 Divalent Mercury }  $\text{Hg}^{ic}$  or  $\text{Hg}^{..}$

Use a solution of Mercuric Chloride ( $\text{HgCl}_2$ ) for wet reactions.

Reagent.	Results observed.	Remarks.
1. $\text{HCl}$	No reaction.	Distinction from $\text{Hg}^{ous}$ Compounds (p. 96).
2. $\text{H}_2\text{S}$ (in presence of $\text{HCl}$ )	A black precipitate of Mercuric Sulphide is obtained, and there is generally a characteristic colour change, the precipitate being at first nearly white, and then changing to yellow, brown, and finally black. $\text{HgCl}_2\text{Aq} + \text{H}_2\text{S} = \text{HgS} + 2\text{HClAq}$	The precipitate first formed is a double compound, e. g. $\text{HgS} \cdot \text{HgCl}_2$ which is decomposed by $\text{H}_2\text{S}$ .
3. $(\text{NH}_4)_2\text{S}$	Black precipitate of Mercuric Sulphide. $\text{HgCl}_2\text{Aq} + (\text{NH}_4)_2\text{SAq} = \text{HgS} + 2\text{NH}_4\text{ClAq}$	
4. $\text{KOH}$ or $\text{NaOH}$	Yellow precipitate of Mercuric Oxide. $\text{HgCl}_2\text{Aq} + 2\text{KOHAq} = \text{HgO} + \text{H}_2\text{O} + 2\text{KClAq}$	Distinction from Mercurous Compounds, which give a black precipitate.
5. $\text{NH}_4\text{OH}$	White precipitate of Dimercur. Ammonium Chloride. $2\text{HgCl}_2\text{Aq} + 2\text{NH}_4\text{OHAq} = \text{NH}_2\text{Hg}_2\text{Cl} + \text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$	(Distinction from $\text{Hg}^{ous}$ Compounds.)
6. $\text{KI}$	Scarlet precipitate of Mercuric Iodide, soluble in excess of the reagent. $\text{HgCl}_2\text{Aq} + 2\text{KIAq} = \text{HgI}_2 + 2\text{KClAq}$ $\text{HgI}_2 + 2\text{KIAq} = \text{HgI}_2 + 2\text{KIAq}$	Distinction from Mercurous Compounds, which give a finch green precipitate.
7. $\text{SnCl}_2$	A white precipitate of Mercurous Chloride is formed, which, if excess of reagent be added, reduces to Metallic Mercury. $a) 2\text{HgCl}_2\text{Aq} + \text{SnCl}_2\text{Aq} = 2\text{HgCl} + \text{SnCl}_4\text{Aq}$ $b) 2\text{HgCl} + \text{SnCl}_2\text{Aq} = 2\text{Hg} + \text{SnCl}_4\text{Aq}$ <div style="display: flex; justify-content: space-around; width: 100%;"> <span>Stannous Chloride</span> <span>Stannic Chloride</span> </div>	
8. $\text{K}_2\text{CrO}_4$	Red precipitate of Mercuric Chromate. $\text{HgCl}_2\text{Aq} + \text{K}_2\text{CrO}_4\text{Aq} = \text{HgCrO}_4 + 2\text{KClAq}$	
9. $\text{Cu}$ (and $\text{HCl}$ )	A strip of Metallic Copper warmed gently with a solution of a Mercury salt acidified by Hydrochloric Acid has a coating of Mercury deposited upon it. On removing the strip after warming for a few minutes, and then rubbing between filter paper, the silvery appearance is very characteristic.	Mercurous Compounds react similarly.
10. $\text{C}$ and $\text{Na}_2\text{CO}_3$	On heating the dry substance mixed with Carbon and Sodium Carbonate in a bulb tube, a sublimate of Mercury is obtained.	do. do.

**Summary regarding Mercury and Mercuric Compounds,**  
most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
Hg	<b>Metallic Mercury</b>	Silvery liquid.	(See p. 97, Hg <sup>ous</sup> ).	
Hg(NO <sub>3</sub> ) <sub>2</sub>	<b>Mercuric Nitrate</b>	White crystalline solid. Decomposes on heating cautiously to give red Oxide of Mercury. $2\text{Hg}(\text{NO}_3)_2 = 2\text{HgO} + 4\text{NO}_2 + \text{O}$	Soluble in water.	1. 2. 3
HgCl <sub>2</sub>	<b>Mercuric Chloride (Corrosive Sublimate)</b>	White solid.	Soluble in water.	1. 2. Heat HgSO <sub>4</sub> and NaCl
HgBr <sub>2</sub>	<b>Mercuric Bromide</b>	White cryst. solid.	Soluble in water.	1. 2
HgI <sub>2</sub>	<b>Mercuric Iodide</b>	Scarlet solid. Changes to allotropic yellow modification on heating.	Insoluble in water. Soluble in concentrated Hydrochloric Acid.	4
HgSO <sub>4</sub>	<b>Mercuric Sulphate</b>	White solid.	Slightly soluble in water.	3
HgCrO <sub>4</sub>	<b>Mercuric Chromate</b>	Red solid.	Insoluble in water. Soluble in acids.	4
Hg(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> or (CH <sub>3</sub> COO) <sub>2</sub> Hg	<b>Mercuric Acetate</b>	White cryst. solid.	Soluble in water.	1. 2
HgO	<b>Mercuric Oxide</b>	Two allotropic modifications:— (a) HgO yellow, obtained by precipitation (p. 68). (b) HgO red solid, obtained by heating the nitrate. Decomposes to Mercury and Oxygen on strongly heating.	Insoluble in water. Soluble in dilute acids.	(a) Yellow (b) Red. Heat nitrate.
HgS	<b>Mercuric Sulphide (ore is called Cinnabar)</b>	Allotropic varieties:— (a) Black powder. (b) Scarlet powder (vermilion). (c) Red solid (cinnabar).	Insoluble in water and dilute acids. Soluble in aqua regia.	(a) 4 (b) Sublimation of Hg and S.

**Alloys :—**Mercury Alloys are termed **Amalgams**.

Sodium Amalgam	Silvery solid which becomes plastic on heating.	Reacts with water, giving off hydrogen.	Direct union.
----------------	-------------------------------------------------	-----------------------------------------	---------------

## Summary of Reactions. Bismuth. Bi.

Use a solution of Bismuth Nitrate,  $\text{Bi}(\text{NO}_3)_3$ , or Bismuth Chloride,  $\text{BiCl}_3$ .

Reagent.	Results observed.	Remarks.
1. HCl	<p>A precipitate of <b>Bismuth Oxychloride</b> (<math>\text{BiOCl}</math>) may form, not due to the HCl, but to the water in which the acid is dissolved. This precipitate dissolves on adding a little more Hydrochloric Acid and warming gently.</p> <p>a) <math>\text{BiCl}_3\text{Aq} + \text{H}_2\text{O} \rightleftharpoons \text{BiOCl} + 2\text{HClAq}</math>  b) <math>\text{BiOCl} + 2\text{HClAq} \rightleftharpoons \text{BiCl}_3\text{Aq} + \text{H}_2\text{O}</math></p>	<p>It is to be noted that equation b) is the converse of equation a). Such a reaction is said to be reversible, because it proceeds in one direction or the other under different conditions. In this particular case the relative proportions of HCl and water are the factors which determine whether a precipitate will form or not.</p>
2. $\text{H}_2\text{S}$ (in presence of HCl)	<p><b>Brownish black precipitate of Bismuth Sulfide</b> (<math>\text{Bi}_2\text{S}_3</math>), soluble in moderately concentrated boiling Nitric Acid.</p> $2\text{Bi}(\text{NO}_3)_3\text{Aq} + 3\text{H}_2\text{S} = \text{Bi}_2\text{S}_3 + 6\text{HNO}_3\text{Aq}.$	
3. $(\text{NH}_4)_2\text{S}$	<p><b>Brownish black precipitate of Bismuth Sulfide</b> (<math>\text{Bi}_2\text{S}_3</math>).</p> $2\text{Bi}(\text{NO}_3)_3\text{Aq} + 3(\text{NH}_4)_2\text{SAq} = \text{Bi}_2\text{S}_3 + 6\text{NH}_4\text{NO}_3\text{Aq}$	
4. KOH, NaOH, or $\text{NH}_4\text{OH}$	<p><b>White precipitate of Bismuth Hydroxide</b> <math>\{\text{Bi}(\text{OH})_3\}</math>  e. g. <math>\text{Bi}(\text{NO}_3)_3\text{Aq} + 3\text{KOH Aq} = \text{Bi}(\text{OH})_3 + 3\text{KNO}_3\text{Aq}</math></p>	
5. Water upon the Chloride	<p>Filter off the precipitate of Bismuth Hydroxide obtained in Expt. 4, wash on the filter so as to get the precipitate into the apex, place the filter funnel in the mouth of a clean empty test-tube, and dissolve the white pp. by addition of a few drops of dilute Hydrochloric Acid dropped on to the Hydroxide. The solution will filter into the test-tube. Fill up the test-tube with water. A precipitate of Bismuth Oxychloride immediately forms.</p> <p>a) <math>\text{Bi}(\text{OH})_3 + 3\text{HClAq} = \text{BiCl}_3\text{Aq} + 3\text{H}_2\text{O}</math>  b) <math>\text{BiCl}_3\text{Aq} + \text{H}_2\text{O} = \text{BiOCl} + 2\text{HClAq}</math></p>	<p>Note.—This reaction may sometimes be obtained on adding water to the original solution, even when a nitrate, by adding Ammonium Chloride and then diluting with water.</p>
6. KI	<p><b>Brown precipitate of Bismuth Iodide</b> (<math>\text{BiI}_3</math>) (soluble in excess to give a brown solution).  <math display="block">\text{Bi}(\text{NO}_3)_3\text{Aq} + 3\text{KIAq} = \text{BiI}_3 + 3\text{KNO}_3\text{Aq}</math></p>	
7. $\text{K}_2\text{CrO}_4\text{Aq}$	<p><b>Reddish precipitate of Bismuth Chromate</b> is formed.</p> $2\text{BiCl}_3\text{Aq} + 3\text{K}_2\text{CrO}_4\text{Aq} = \text{Bi}_2(\text{CrO}_4)_3 + 6\text{KClAq}$ <p style="text-align: center;">Bismuth Chromate</p>	
8. C	Heated on Charcoal a <b>brittle bead of metallic Bismuth</b> is obtained.	
9. Flame test	Heated on Platinum wire gives a blue flame.	Bismuth rapidly corrodes Platinum, so that the test is better avoided.



## Summary regarding Bismuth and notable Bismuth Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
Bi	<b>Metallic Bismuth</b> , m. pt. 270° C.	Nearly white metal with peculiar lustre.	Insol. in HClAq and in H <sub>2</sub> SO <sub>4</sub> Aq, but soluble in HNO <sub>3</sub> Aq. Bi + 4HNO <sub>3</sub> Aq = Bi(NO <sub>3</sub> ) <sub>3</sub> Aq + 2H <sub>2</sub> O + NO	Reduction on Carbon.
Bi(NO <sub>3</sub> ) <sub>3</sub>	<b>Bismuth Nitrate</b>	White crystalline solid; brown fumes on heating.	Reacts with water to give a white precipitate of Basic Nitrate, Bi(OH) <sub>2</sub> .NO <sub>3</sub> . Soluble in HNO <sub>3</sub> Aq or HClAq.	1. 2. 3
Bi(OH) <sub>2</sub> .NO <sub>3</sub>	<b>Basic Bismuth Nitrate</b>	White solid.	Insoluble in water. Soluble in Nitric Acid.	4
BiCl <sub>3</sub>	<b>Bismuth Oxynitrate</b> <b>Bismuth Chloride</b>	White cryst. solid.	Reacts with water to give the Oxychloride. Soluble in HClAq or HNO <sub>3</sub> Aq.	1. 2
BiOCl	<b>Bismuth Oxychloride</b>	White solid.	Insoluble in water. Soluble in Hydrochloric Acid.	4
BiBr <sub>3</sub>	<b>Bismuth Bromide</b>	White solid.	Reacts with water.	1. 2
BiI <sub>3</sub>	<b>Bismuth Iodide</b>	Brown solid.	Insoluble in water. Soluble in Potassium Iodide and in acids.	4
Bi <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	<b>Bismuth Carbonate</b> (a basic salt)	White solid.	Insoluble in water. Soluble in acids with decomposition.	4
Bi <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	<b>Bismuth Sulphate</b>	White solid.	Slightly soluble in water. Soluble in acids.	1. 2
BiPO <sub>4</sub>	<b>Bismuth Phosphate</b>	White solid.	Insoluble in water. Soluble in acids.	4
Bi <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub>	<b>Bismuth Chromate</b>	Reddish solid.	do. do.	4
Bi <sub>2</sub> S <sub>3</sub>	<b>Bismuth Sulphide</b>	Brownish black solid.	Insoluble in water. Soluble in moderately concentrated boiling Nitric Acid.	4
Bi(OH) <sub>3</sub>	<b>Bismuth Hydroxide</b>	White solid.	Insoluble in water. Soluble in acids.	4
Bi <sub>2</sub> O <sub>3</sub>	<b>Bismuth Oxide</b>	Nearly white solid, turns brown on heating.	do. do.	Heat Hydroxide or Carbonate.

Alloy :—Fusible Metal, Bi. Pb. Sn.

## Group II b. As. Sb. Sn<sup>ous</sup>. Sn<sup>ic</sup>. Summary of Reactions. Arsenious and Arsenic Compounds.

For reactions of **Arsenious Compounds** use a solution of **Arsenious Oxide** in **Hydrochloric Acid**, or of **Sodium Arsenite**.

For **Arsenic Compounds** use a solution of **Sodium Arsenate**.

Reagent.	Arsenious Compounds.	Arsenic Compounds.
1. HCl	No reaction.	1) No reaction.
2. H <sub>2</sub> S in presence of HCl	<p><b>Yellow precipitate of Arsenious Sulphide.</b></p> $2\text{AsCl}_3\text{Aq} + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 6\text{HClAq}$ <p>The precipitate is soluble in :</p> <p>a) (NH<sub>4</sub>)<sub>2</sub>S ;</p> <p>b) (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>—<b>Distinction from Antimony ;</b></p> <p>c) KOHAq or NaOHAq.</p> <p>d) <b>Insoluble in conc. HCl—Distinction from Sb.</b></p> <p>a) The solution in yellow (NH<sub>4</sub>)<sub>2</sub>S, which has Sulphur in solution, contains Ammonium Thioarsenate.</p> $\text{As}_2\text{S}_3 + 3(\text{NH}_4)_2\text{SAq} + 2\text{S} = \frac{2(\text{NH}_4)_3\text{AsS}_4\text{Aq}}{\text{Ammon. Thioarsenate}}$ <p>On addition of HClAq or K<sub>2</sub>SO<sub>4</sub>Aq to the solution Arsenic Pentasulphide is thrown down.</p> $2(\text{NH}_4)_3\text{AsS}_4 + 6\text{HClAq} = 6\text{NH}_4\text{ClAq} + 3\text{H}_2\text{S} + \text{As}_2\text{S}_5$ <p>b) The solution in Ammon. Carbonate contains Ammon. Arsenite and Ammon. Thioarsenite.</p> $\text{As}_2\text{S}_3 + (3\text{NH}_4)_2\text{CO}_3 = \frac{(\text{NH}_4)_3\text{AsO}_3\text{Aq}}{\text{Ammon. Arsenite}} + \frac{(\text{NH}_4)_3\text{AsS}_3\text{Aq}}{\text{Ammon. Thioarsenite}} + 3\text{CO}_2$ <p>c) The solution in KOHAq or NaOHAq contains Sodium or Potassium Arsenite and Thioarsenite.</p> $\text{As}_2\text{S}_3 + 6\text{KOHAq} = \text{K}_3\text{AsO}_3\text{Aq} + \text{K}_3\text{AsS}_3\text{Aq} + 3\text{H}_2\text{O}$	<p>2) Arsenic Compounds give <b>no precipitate with Sulphuretted Hydrogen</b> until reduced to the Arsenious condition. This is effected with considerable difficulty by the action of H<sub>2</sub>S on the warm solution (e.g.</p> $\text{Na}_2\text{HAsO}_4 + \text{H}_2\text{S} = \text{Na}_2\text{HASO}_3 + \text{H}_2\text{O} + \text{S},$ <p>but much more readily by Sulphurous Acid solution.</p> $\text{Na}_2\text{HASO}_4 + \text{H}_2\text{SO}_3\text{Aq} \xrightarrow{\text{Sod. Hyd. Arsenate}} \text{Na}_2\text{HASO}_3 + \text{H}_2\text{SO}_4\text{Aq}$ <p>Sod. Hyd. Arsenite</p> <p>N.B. To effect the reduction boil up with Sulphurous Acid solution and then pass Sulphuretted Hydrogen through it.</p> $\text{Na}_2\text{HASO}_3 + \text{H}_2\text{SO}_4\text{Aq} = \text{Na}_2\text{SO}_4\text{Aq} + \text{H}_3\text{AsO}_3$ $2\text{H}_3\text{AsO}_3 + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 6\text{H}_2\text{O}$
3. (NH <sub>4</sub> ) <sub>2</sub> S	No precipitate.	3) No precipitate.
4. KOH, NaOH, or NH <sub>4</sub> OH	<p><b>No precipitate — Distinction from Antimony.</b></p>	4) do.

**Group II b. As. Sb. Sn<sup>ous</sup>. Sn<sup>ic</sup>. Summary of Reactions.**  
**Arsenious and Arsenic Compounds** (*continued*).

For reactions of **Arsenious Compounds** use a solution of **Arsenious Oxide** in **Hydrochloric Acid**, or of **Sodium Arsenite**.

For **Arsenic Compounds** use a solution of **Sodium Arsenate**.

Reagent.	Arsenious Compounds.	Arsenic Compounds.
5. <b>Cu</b> (and HCl)	<p><b>Reinsch's Test.</b> Acidify about 10 c.c. of solution with HClAq, add a strip of Copper, and boil for a few minutes. A greyish deposit of Arsenic comes down on the Copper.</p> $3\text{Cu} + 2\text{AsCl}_3\text{Aq} = 3\text{CuCl}_2\text{Aq} + 2\text{As}$ <p>Remove the strip, wash with distilled water, dry carefully between folds of filter paper, and heat in small dry tube of hard glass, closing the end with the thumb. Transparent glancing crystals of Arsenious Oxide deposit on glass above heated area. Examine with a lens.</p>	<p>5) <b>Reinsch's Test.</b> This test only takes place after reduction of Arsenic Compounds to Arsenious condition. This is readily effected by boiling with Sulphurous Acid solution before adding the Copper and Hydrochloric Acid.</p>
6. <b>CuSO<sub>4</sub></b>	<p>Make solution neutral before adding reagent. Bright green precipitate of Scheele's green (CuHAsO<sub>3</sub>).</p> $\text{CuSO}_4\text{Aq} + \text{Na}_2\text{HAsO}_3\text{Aq} = \text{CuHAsO}_3 + \text{Na}_2\text{SO}_4\text{Aq}$	6)
7. <b>AgNO<sub>3</sub></b>	<p>With neutral solution a <b>yellow</b> precipitate of <b>Silver Arsenite</b>, Ag<sub>3</sub>AsO<sub>3</sub>, is obtained.</p> $6\text{AgNO}_3\text{Aq} + 3\text{Na}_2\text{HAsO}_3\text{Aq} = 2\text{Ag}_3\text{AsO}_3 + 6\text{NaNO}_3\text{Aq} + \text{H}_3\text{AsO}_3$	<p>7) Reddish brown precipitate of <b>Silver Arsenate</b> comes down from neutral solutions.</p> $6\text{AgNO}_3\text{Aq} + 3\text{Na}_2\text{HAsO}_4\text{Aq} = 2\text{Ag}_3\text{AsO}_4 + 6\text{NaNO}_3\text{Aq} + \text{H}_3\text{AsO}_4$
8. <b>Heated on Charcoal</b>	<p>} White fumes—garlic odour.</p>	8) Same as Arsenious Compounds.
9. <b>Reduction by C in tube</b>	<p>Heat a small quantity of dry powdered substance mixed with powdered Carbon and Na<sub>2</sub>CO<sub>3</sub> in hard glass tube. A grey mirror of Arsenic is generally obtained above heated area. The mirror is soluble in bleaching powder :—<b>Distinction from Antimony.</b></p>	9) do. do.
10. <b>Marsh's Test</b>	<p>} These are delicate reduction tests, by which traces of Arsenic can be detected. They are rarely necessary in Elementary Analysis (see p. 108).</p>	10) do. do.
11. <b>Gutzeit's Test</b>		11) do. do.

### The Marsh and Gutzeit Tests for Arsenic and Antimony.

**Marsh's Test.** Place in a Woulff's bottle about 10 grams of pure zinc, cover with water, and add a few c.c. of pure sulphuric acid. Hydrogen is evolved. The Woulff's bottle is connected with a tube containing granular calcium chloride to dry the gas, and then with a narrow tube of hard glass (say 3-4 mm. diameter) about 6 inches long, which is constricted in the middle, and drawn out and bent up to form a jet at the free end. When the air has presumably been expelled, light the jet and heat the hard glass tube just before the constriction. If after heating for 10 minutes no film of arsenic is deposited near the constriction, the chemicals may be assumed to be pure. Now add, say, 10-15 c.c. of solution which is to be tested to the reaction mixture, while continuing to heat near the constriction. If a deposit appears it may consist of arsenic or antimony. To distinguish between the two, cut off the tube at the constriction and put the portion with the deposit upon it into a small basin containing fresh bleaching powder solution. The arsenic deposit rapidly dissolves, while that due to antimony is only slightly affected.

**Gutzeit's Test.** Heat a small quantity of the substance with  $\text{NaOH}_{\text{Aq}}$  or  $\text{KOH}_{\text{Aq}}$  and pure Zinc. If Arsenic be present  $\text{AsH}_3$  is evolved, which colours yellow a piece of filter paper moistened with  $\text{HgCl}_2_{\text{Aq}}$ , and held in the mouth of the tube.

## Summary regarding Arsenic and its notable Compounds.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of pre-paration.
As	<b>Metallic Arsenic</b>	Greyish solid with metallic lustre.	Insoluble in water and HClAq. Oxidized and dissolved by $\text{HNO}_3\text{Aq}$ . $\text{As} + 3\text{HNO}_3\text{Aq} = \text{H}_3\text{AsO}_4 + 2\text{NO}_2 + \text{NO}$	Reduction of $\text{As}_2\text{O}_3$ with C in tube.
<b>A. ARSENIOS COMPOUNDS.</b>				
(AsCl <sub>3</sub> )	Arsenious Chloride	Poisonous liquid.	Soluble in Hydrochloric Acid.	Direct union of elements.
As <sub>2</sub> O <sub>3</sub>	<b>Arsenious Oxide</b> (White Arsenic)	White solid.	Slightly soluble in water: more soluble in HClAq.	
As <sub>2</sub> S <sub>2</sub>	<b>Realgar</b> (native compound)	Reddish solid.	Soluble in HClAq and KClO <sub>3</sub> or in Nitric Acid.	do.
As <sub>2</sub> S <sub>3</sub>	<b>Arsenious Sulphide</b> (nativesubs. is called <b>Orpiment</b> )	Yellow solid.	Insoluble in water and HClAq (Note—Sb <sub>2</sub> S <sub>3</sub> is readily soluble in conc. HCl). Dissolves in HCl and KClO <sub>3</sub> or in aqua regia. The minimum quantity of HNO <sub>3</sub> should be employed, when a small quantity of H <sub>2</sub> S will come off, and H <sub>2</sub> SO <sub>4</sub> will be found in solution.	
Na <sub>2</sub> HAsO <sub>3</sub>	<b>Sodium Arsenite</b>	White solid.	Soluble in water.	1
K <sub>2</sub> HAsO <sub>3</sub>	<b>Potassium Arsenite</b>	do.	do.	1
CuHAsO <sub>3</sub>	<b>Copper Hydrogen Arsenite</b> (Scheele's green)	Bright green solid.	Insoluble in water. Soluble in acids.	4
Ag <sub>3</sub> AsO <sub>2</sub>	<b>Silver Arsenite</b>	Light yellow solid.	do. do.	4
<b>B. ARSENIC COMPOUNDS.</b>				
As <sub>2</sub> O <sub>5</sub>	<b>Arsenic Pentoxide</b>	White solid.	Sol. in water to give Arsenic Acid.	Heat $\text{H}_3\text{AsO}_4$ .
H <sub>3</sub> AsO <sub>4</sub>	<b>Arsenic Acid</b>	do.	Sol. in water.	Oxidize $\text{As}_2\text{O}_3$ by $\text{HNO}_3$ .
Na <sub>2</sub> HAsO <sub>4</sub>	<b>Sodium Hydrogen Arsenate</b>	do.	do.	1
K <sub>2</sub> HAsO <sub>4</sub>	<b>Potassium Hydrogen Arsenate</b>	do.	do.	1
Ag <sub>3</sub> AsO <sub>4</sub>	<b>Silver Arsenate</b>	Reddish brown solid.	Insol. in water. Soluble in acids.	4
As <sub>2</sub> S <sub>5</sub>	<b>Arsenic Penta-sulphide</b>	Yellow solid.	Sol. in aqua regia.	4

## Summary of Reactions. Antimony in Antimonious condition ( $\text{Sb}^{\cdots}$ ) with a note on Antimonic Compounds.

Use a solution of Antimonious Chloride ( $\text{SbCl}_3$ ) in dilute Hydrochloric Acid.

Reagent.	Antimonious Compounds.	Antimonic Compounds.
1. HCl	A white precipitate of <b>Antimony Oxychloride</b> ( $\text{SbOCl}$ ) may be formed, which dissolves on adding a little more $\text{HClAq}$ and warming. The reaction is reversible. $\text{SbCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{SbOCl} + 2\text{HCl}$	<p>Note. Antimonic Compounds would rarely be met with in elementary analysis. On warming powdered Antimony with Nitric Acid, Metantimonic Acid is formed (<math>\text{HSbO}_3</math>), which dissolves in conc. HCl with addition of a crystal of Potassium Chlorate to form a solution which would give the tests summarized under Antimonious Compounds.</p>
2. $\text{H}_2\text{S}$ (in presence of HCl)	<b>Orange precipitate of Antimonious Sulphide</b> ( $\text{Sb}_2\text{S}_3$ ). $2\text{SbCl}_3 + 3\text{H}_2\text{S} = \text{Sb}_2\text{S}_3 + 6\text{HClAq}$ <p>The precipitate is <i>a</i>) soluble in yellow Ammonium Sulphide; <i>b</i>) insoluble in Ammonium Carbonate (Distinction from Arsenic); <i>c</i>) soluble in KOH or NaOH; <i>d</i>) soluble in <math>\text{HClAq}</math>—Distinction from As.</p> <p><i>a</i>) Ammonium Thioantimoniate is formed.  <math display="block">\text{Sb}_2\text{S}_3 + 3(\text{NH}_4)_2\text{SAq} + 2\text{S} = 2(\text{NH}_4)_3\text{SbS}_4\text{Aq}</math> <p style="text-align: center;">Ammon. Thioantimoniate</p> <p>On addition of <math>\text{HClAq}</math> or <math>\text{H}_2\text{SO}_4\text{Aq}</math>, Antimony Pentasulphide is precipitated.  <math display="block">2(\text{NH}_4)_3\text{SbS}_4 + 6\text{HClAq} = 6\text{NH}_4\text{ClAq} + \text{Sb}_2\text{S}_5 + 3\text{H}_2\text{S}</math></p> <p><i>c</i>) <math display="block">\text{Sb}_2\text{O}_3 + 2\text{NaOHAq} = 2\text{SbO}(\text{ONa}) + \text{H}_2\text{O}</math> <p style="text-align: center;">Sodium Met- antimoniate</p></p> <p><i>d</i>) <math display="block">\text{Sb}_2\text{S}_3 + 6\text{HClAq} = 2\text{SbCl}_3\text{Aq} + 3\text{H}_2\text{S} \nearrow</math></p></p>	
3. $(\text{NH}_4)_2\text{S}$	No precipitate.	
4. KOH, NaOH, or $\text{NH}_4\text{OH}$	<b>White precipitate of Antimonious Oxide</b> may be obtained—Distinction from Arsenic. $2\text{SbCl}_3 + 6\text{NH}_4\text{OHAq} = \text{Sb}_2\text{O}_3 + 3\text{H}_2\text{O} + 6\text{NH}_4\text{ClAq}$ <p>As many metallic compounds give a white precipitate with KOH or <math>\text{NH}_4\text{OH}</math> it is advisable to confirm further. Filter, wash, dissolve the precipitate in a few drops of <math>\text{HClAq}</math>, and add the solution to about 50 c.c. of water. A white precipitate of Antimony Oxychloride (<math>\text{SbOCl}</math>) comes down, soluble in Tartaric Acid.</p>	
5. Metallic Copper (and HCl)	<b>Reinsch's Test.</b> Add a few drops of $\text{HClAq}$ to 10 c.c. of solution, and heat for a few minutes with a strip of Copper. Remove the strip, dry, and heat in a small tube. Amorphous white sublimate.	
6. Reduction in bulb tube	Heat a small quantity of dry powdered substance mixed with Carbon and Sodium Carbonate in a hard glass tube. A brilliant sublimate forms. By means of a file break off the tube, and put portion with sublimate in $\text{H}_2\text{SAq}$ —orange precipitate forms.	
7. Carbon	Antimony Compounds reduce to give brittle beads, which readily oxidize giving white fumes.	
8. Marsh's Test	Similar to test for Arsenic (p. 108).	

**Summary regarding Antimony and its notable Compounds,**  
most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
<b>Sb</b>	<b>Metallic Antimony</b>	Brilliant silvery lustre, brittle.	Nearly insoluble in Hydrochloric Acid. Dissolves in concentrated Hydrochloric Acid to which a few crystals of Potassium Chlorate have been added. On adding the solution to water, Antimony Oxychloride is precipitated, soluble in Tartaric Acid.	Reduction with Carbon.
<b>SbCl<sub>3</sub></b>	<b>Antimonious Chloride</b>	White soft solid.	Gives a white precipitate of Antimony Oxychloride with water, but is soluble in dilute Hydrochloric Acid.	Direct union.
<b>SbOCl</b>	<b>Antimony Oxychloride</b>	White powder.	Insoluble in water, soluble in Hydrochloric Acid.	4
<b>SbCl<sub>5</sub></b>	<b>Antimony Pentachloride</b> (Antimonic Chloride)	Yellowish liquid.	Decomposed by water.	Direct union.
<b>Sb<sub>2</sub>O<sub>3</sub></b>	<b>Antimonious Oxide</b>	White solid.	Insoluble in water. Soluble in Hydrochloric Acid.	Direct union or 4
( <b>Sb<sub>2</sub>O<sub>4</sub></b> )	Antimony Tetroxide	White solid.	Nearly insoluble.)	
<b>Sb<sub>2</sub>O<sub>5</sub></b>	<b>Antimony Pentoxide</b>	do.	Dissolves in conc. HCl with a few crystals of HClO <sub>3</sub> (or in aqua regia, using only a few drops of HNO <sub>3</sub> ).	Heat H <sub>2</sub> SbO <sub>3</sub> .
<b>HSbO<sub>3</sub></b>	Metantimonic Acid	do.	do. do.	Oxidize Sb by HNO <sub>3</sub> .
<b>KSbO<sub>3</sub></b>	Potassium Metantimoniate	do.	Slightly soluble in water on boiling.	
<b>NaSbO<sub>3</sub></b>	Sodium Metantimoniate	do.	Nearly insoluble in water.	4
<b>Sb<sub>2</sub>S<sub>3</sub></b>	<b>Antimonious Sulphide</b>	The naturally occurring substance (Stibnite) has either a grey metallic lustre, or is nearly black. The substance obtained by precipitation is orange.	Insoluble in water. Soluble in Ammonium Sulphide (p. 110). Soluble in concentrated HCl with evolution of H <sub>2</sub> S. Sb <sub>2</sub> S <sub>3</sub> + 6HCl = 2SbCl <sub>3</sub> + 3H <sub>2</sub> S	4
<b>Sb<sub>2</sub>S<sub>5</sub></b>	Antimony Pentasulphide	Orange yellow solid.	Soluble in concentrated Hydrochloric Acid.	4
<b>K.SbO.C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.½H<sub>2</sub>O</b> <b>Tartar Emetic</b>		White crystalline solid.	Soluble in water.	1

# Summary of Reactions. Tin. Sn. { a) Stannous. Sn<sup>++</sup>. b) Stannic. Sn<sup>+++</sup>.

Use a solution of **Stannous Chloride** (SnCl<sub>2</sub>) for Stannous Compounds and a solution of **Stannic Chloride** (SnCl<sub>4</sub>) for Stannic Compounds.

Reagent.	Stannous Compounds. Results.	Stannic Compounds. Results.
1. HCl	No precipitate.	1) No precipitate.
2. H <sub>2</sub> S (in presence of HCl)	<b>Brownish precipitate of Stannic Sulphide</b> (SnS) — Distinction from Stannic. $\text{SnCl}_2\text{Aq} + \text{H}_2\text{S} = \text{SnS} + 2\text{HClAq}$ The precipitate is soluble in yellow Ammonium Sulphide, (NH <sub>4</sub> ) <sub>2</sub> S. $\text{SnS} + (\text{NH}_4)_2\text{SAq} + \text{S} = (\text{NH}_4)_2\text{SnS}_3\text{Aq}$ <div style="text-align: center;">Ammon. Thiostannate</div> The Ammonium Thiostannate is easily decomposed by HClAq or H <sub>2</sub> SO <sub>4</sub> Aq with precipitation of yellow Stannic Sulphide (SnS <sub>2</sub> ). $(\text{NH}_4)_2\text{SnS}_3 + 2\text{HClAq} = \text{SnS}_2 + \text{H}_2\text{S} + 2\text{NH}_4\text{ClAq}$	2) A <b>yellow precipitate of Stannic Sulphide</b> (SnS <sub>2</sub> ) is obtained — Distinction from Stannous. $\text{SnCl}_4\text{Aq} + 2\text{H}_2\text{S} = \text{SnS}_2 + 4\text{HClAq}$ The precipitate is soluble in (NH <sub>4</sub> ) <sub>2</sub> SAq, forming Ammonium Thiostannate. $\text{SnS}_2 + (\text{NH}_4)_2\text{SAq} = (\text{NH}_4)_2\text{SnS}_3\text{Aq}$ This solution is decomposed by acids as described under Stannous Compounds.
3. HgCl <sub>2</sub>	A white precipitate of <b>Mercurous Chloride</b> (HgCl) is formed, and if excess of Stannous Chloride be present a <b>greyish precipitate of Mercury</b> is ultimately obtained. a) $\text{SnCl}_2\text{Aq} + 2\text{HgCl}_2\text{Aq} = 2\text{HgCl} + \text{SnCl}_4\text{Aq}$ b) $\text{SnCl}_2\text{Aq} + 2\text{HgCl} = 2\text{Hg} + \text{SnCl}_4\text{Aq}$	3) <b>No reaction. Important Distinction between Stannous and Stannic Compounds.</b>
4. KOH, NaOH, or NH <sub>4</sub> OH	<b>White precipitate of Stannous Hydroxide</b> , Sn(OH) <sub>2</sub> . $\text{SnCl}_2\text{Aq} + 2\text{KOH Aq} = \text{Sn(OH)}_2 + 2\text{KClAq}$ The precipitate is soluble in excess of reagent, forming Stannite. $\text{Sn(OH)}_2 + 2\text{KOH Aq} = \text{K}_2\text{SnO}_2\text{Aq} + 2\text{H}_2\text{O}$ <div style="text-align: center;">Potassium Stannite</div>	4) <b>White precipitate of Stannic Hydroxide</b> , Sn(OH) <sub>4</sub> , soluble in excess.
5. Zn (and HCl)	<b>Metallic Tin</b> is deposited and can be separated and dissolved by boiling with Hydrochloric Acid. Then add Mercuric Chloride (HgCl <sub>2</sub> ). — Test 3 above. $\text{SnCl}_2\text{Aq} + \text{Zn} = \text{Sn} + \text{ZnCl}_2\text{Aq}$	5) <b>Stannic Compounds are reduced</b> to Stannous by nascent hydrogen, and the Stannous reactions can then be obtained, e.g. reaction with Mercuric Chloride.
6. Reduction on Carbon	Mix the powdered substance with about double the quantity of a mixture of <b>Potassium Cyanide and Borax</b> and heat strongly in reducing flame. A bright bead of Tin will be obtained with some difficulty. To confirm Tin from this process boil up the residue with water, separate off globules of Tin, and dissolve by boiling with a small quantity of conc. HCl. Dilute somewhat and then add HgCl <sub>2</sub> and warm. (See Test 3 above for result.)	6) Similar to Stannous.
7. Co(NO <sub>3</sub> ) <sub>2</sub> and ignition	Moisten filter paper with a concentrated solution and then with Co(NO <sub>3</sub> ) <sub>2</sub> and burn the paper. A <b>bluish-green residue</b> is left.	7) Similar to Stannous.



**Summary regarding Tin and its notable Compounds,**  
most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of pre-paration.
Sn	<b>Metallic Tin</b> , m. pt. 233° C.	Met with in different forms, e. g. sticks, granulated, foil, &c.	Soluble in Hydrochloric Acid (conc.). $\text{Sn} + 2\text{HClAq} = \text{SnCl}_2\text{Aq} + \text{H}_2$ Stannous Chloride.	Reduction of Carbon.
<b>A. STANNOUS COMPOUNDS.</b>				
$\text{SnCl}_2$	<b>Stannous Chloride</b>	Nearly white cryst. solid (faint yellowish tint usually noticeable).	Soluble in Hydrochloric Acid. A basic salt is precipitated with water, $\text{Sn} \begin{smallmatrix} \text{OH} \\ \text{Cl} \end{smallmatrix}$ . This basic salt may form after prolonged exposure of the dry salt to air.	3
$\text{SnSO}_4$	<b>Stannous Sulphate</b>	White solid.	Soluble in water.	1
( $\text{SnO}$ )	<b>Stannous Oxide</b>	Black solid.	Soluble in acids.	Heat Stannous Oxalate.)
$\text{Sn}(\text{OH})_2$	<b>Stannous Hydroxide</b>	White solid.	Soluble in acids and also in alkaline hydroxides.	4
$\text{SnS}$	<b>Stannous Sulphide</b>	Brownish black or dark grey solid.	Soluble in concentrated Hydrochloric Acid with evolution of $\text{H}_2\text{S}$ .	4
<b>B. STANNIC COMPOUNDS.</b>				
$\text{SnCl}_4$	<b>Stannic Chloride</b>	The pure substance is a fuming liquid decomposed by water.	Soluble in Hydrochloric Acid.	Direct union.
$\text{Sn}(\text{SO}_4)_2$	<b>Stannic Sulphate</b>	White solid.	Soluble in acids.	
$\text{SnS}_2$	<b>Stannic Sulphide</b> (Bronze powder, Mosaic Gold)	Golden yellow solid. May be met with in powder or crystalline scales similar to Lead Iodide.	Insoluble in water and in Hydrochloric Acid. Soluble in conc. $\text{HCl}$ to which a few drops of $\text{HNO}_3$ have been added. With $\text{Zn}$ and $\text{HClAq}$ it gives off $\text{H}_2\text{S}$ .	4
$\text{SnO}_2$	<b>Stannic Oxide</b> (Tin-stone, Putty powder, Cassiterite)	White solid.	Insoluble in water and acids. It can be reduced with $\text{KCN}$ and Borax as described on p. 112.	Tin and $\text{HNO}_3$ .
$\text{Na}_2\text{SnO}_3$	<b>Sodium Stannate</b>	White solid.	Substance met with is generally partially soluble in water.	Fuse $\text{Sn}_2\text{O}$ and $\text{Na}_2\text{CO}$ .

Group III. Al. Fe<sup>ous</sup>. Fe<sup>ic</sup>. (Cr.)Summary of Reactions. Aluminium. Al<sup>+++</sup>.

Use a solution of Aluminium Sulphate or of Alum.

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	
2. H <sub>2</sub> S (in presence of HCl)	No precipitate.	
3. NH <sub>4</sub> OH	White gelatinous precipitate of Aluminium Hydroxide, Al(OH) <sub>3</sub> . $\text{Al}_2(\text{SO}_4)_3\text{Aq} + 6\text{NH}_4\text{OHAq}$ <div style="text-align: center;"> <u>Aluminium Sulphate</u>  <math>= 2\text{Al}(\text{OH})_3 + 3(\text{NH}_4)_2\text{SO}_4\text{Aq}</math> <u>Aluminium Hydroxide</u> </div>	
4. KOH or NaOH	White gelatinous precipitate soluble in excess. $\text{Al}_2(\text{SO}_4)_3\text{Aq} + 6\text{KOH}\text{Aq} = 2\text{Al}(\text{OH})_3 + 3\text{K}_2\text{SO}_4\text{Aq}$ With excess of reagent the precipitate dissolves to form Aluminate. $\text{Al}(\text{OH})_3 + 3\text{KOH}\text{Aq} = \text{Al}(\text{OK})_3\text{Aq} + 3\text{H}_2\text{O}$ <div style="text-align: center;"> <u>Potassium Aluminate</u> </div>	
5. (NH <sub>4</sub> ) <sub>2</sub> S	White gelatinous precipitate of Aluminium Hydroxide, Al(OH) <sub>3</sub> . One might expect to get Aluminium Sulphide, Al <sub>2</sub> S <sub>3</sub> , but that substance is at once decomposed by water, forming the Hydroxide and H <sub>2</sub> S. The two part equations a) and b), or the single equation c), obtained from them by addition, may be used to explain this reaction. a) $\text{Al}_2(\text{SO}_4)_3\text{Aq} + 3(\text{NH}_4)_2\text{SAq}$ $= \text{Al}_2\text{S}_3 + 3(\text{NH}_4)_2\text{SO}_4\text{Aq}$ b) $\text{Al}_2\text{S}_3 + 6\text{H}_2\text{O} = 3\text{H}_2\text{S} + 2\text{Al}(\text{OH})_3$ c) $\text{Al}_2(\text{SO}_4)_3\text{Aq} + 3(\text{NH}_4)_2\text{SAq} + 6\text{H}_2\text{O}$ $= 2\text{Al}(\text{OH})_3 + 3(\text{NH}_4)_2\text{SO}_4\text{Aq} + 3\text{H}_2\text{S} \nearrow$	Free acids should not be present.
6. Co(NO <sub>3</sub> ) <sub>2</sub> and ignite	Heat original substance on Carbon in oxidizing flame and then moisten with Cobalt Nitrate and reheat for some time. A bright blue mass is obtained.	Phosphates, borates, and arsenates may give a similar sort of blue mass, but in these cases the masses can generally be fused. The masses obtained from Aluminium Compounds are infusible if Compounds of other elements are not present.

## Summary regarding Aluminium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
Al	<b>Metallic Aluminium,</b> m. pt. about 650°C.	Brilliant silvery metal. Met with as foil, sheet, wire, turnings, &c.	Soluble in Hydrochloric Acid or Sulphuric Acid; nearly insoluble in Nitric Acid.	Electrolysis.
AlCl <sub>3</sub>	<b>Aluminium Chloride</b>	White deliquescent solid. Fumes in air.	Soluble in water with evolution of heat.	3
AlBr <sub>3</sub>	Aluminium Bromide	do.	do.	3
Al(NO <sub>3</sub> ) <sub>3</sub>	Aluminium Nitrate	White solid.	Soluble in water.	1
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	<b>Aluminium Sulphate</b>	do.	do.	1
K <sub>2</sub> SO <sub>4</sub> . Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 24H <sub>2</sub> O or KAl(SO <sub>4</sub> ) <sub>2</sub> . 12H <sub>2</sub> O	Potash Alum	} White cryst. solid.	do.	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> . Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 24H <sub>2</sub> O or NH <sub>4</sub> . Al(SO <sub>4</sub> ) <sub>2</sub> . 12H <sub>2</sub> O	Ammonia Alum			
AlPO <sub>4</sub>	<b>Aluminium Phosphate</b>	White powder.	Insoluble in water; soluble in acids.	4
Al <sub>4</sub> C <sub>3</sub>	<b>Aluminium Carbide</b>	Greyish powder.	Reacts with water to give Methane. $\text{Al}_4\text{C}_3 + 6\text{H}_2\text{O} = 3\text{CH}_4 + 2\text{Al}_2\text{O}_3$	
Al(OH) <sub>3</sub>	<b>Aluminium Hydroxide</b>	White solid.	Insoluble in water. Easily soluble in acids (and also in KOH or NaOH).	4
Al(ONa) <sub>3</sub>	Sodium Aluminate	White solid.	Soluble in water. Solution is strongly alkaline in reaction.	
Al <sub>2</sub> O <sub>3</sub>	<b>Aluminium Oxide (Alumina).</b> The hydrated Oxide occurring native is the important ore Bauxite	Met with in different forms — corundum, emery, &c.	Insoluble in water. May be easily soluble or almost insoluble in acids, depending upon the source and temperature to which it may have been exposed.	Heat Al(OH) <sub>3</sub> .

Alloys:—Aluminium Bronze, Al (5-12 %): Cu.  
Magnalium, Al (70-94 %): Mg.

# Summary of Reactions for Iron Compounds { <sup>a</sup> Ferrous. <sup>b</sup> Ferric.

For reactions of Ferrous Salts use a solution of Ferrous Sulphate and for reactions of Ferric Salts use a solution of Ferric Chloride.

Reagents.	Ferrous Iron, Fe <sup>++</sup> .	Ferric Iron, Fe <sup>+++</sup> .	Remarks.
1. HCl 2. H <sub>2</sub> S (in presence of HCl)	No precipitate. No action.	1) No precipitate. 2) Ferric Salts are reduced to Ferrous Salts by Sulphuretted Hydrogen. $2\text{FeCl}_3\text{Aq} + \text{H}_2\text{S} = 2\text{FeCl}_2\text{Aq} + 2\text{HCl} + \text{S}$	
3. (NH <sub>4</sub> ) <sub>2</sub> S	Black precipitate of Ferrous Sulphide (FeS). $\text{FeSO}_4\text{Aq} + (\text{NH}_4)_2\text{S} = \text{FeS} + (\text{NH}_4)_2\text{SO}_4\text{Aq}$	3) Black precipitate consisting chiefly of a mixture of Ferrous Sulphide and Sulphur $2\text{FeCl}_3\text{Aq} + 3(\text{NH}_4)_2\text{SAq} = 2\text{FeS} + \text{S} + 6\text{NH}_4\text{ClAq}$	
4. NH <sub>4</sub> OH, KOH, or NaOH	Greenish precipitate of Ferrous Hydroxide, Fe(OH) <sub>2</sub> , which slowly turns brown on the top because of the formation of Ferric Hydroxide on oxidation by the oxygen of the air. a) $\text{FeSO}_4\text{Aq} + 2\text{NH}_4\text{OHAq} = \text{Fe}(\text{OH})_2 + (\text{NH}_4)_2\text{SO}_4\text{Aq}$ Ferrous Hydroxide The oxidation might be expressed by an equation. b) $2\text{Fe}(\text{OH})_2 + \text{O} + \text{H}_2\text{O} = 2\text{Fe}(\text{OH})_3$ Ferric Hydroxide	4) Brown precipitate of Ferric Hydroxide, Fe(OH) <sub>3</sub> . $\text{FeCl}_3\text{Aq} + 3\text{NH}_4\text{OHAq} = \text{Fe}(\text{OH})_3 + 3\text{NH}_4\text{ClAq}$ Ferric Hydroxide	
5. K <sub>4</sub> Fe(CN) <sub>6</sub>	Light blue precipitate consisting of slightly oxidized Potassium Ferrous Ferrocyanide. $\text{FeSO}_4\text{Aq} + \text{K}_4\text{Fe}(\text{CN})_6\text{Aq} = \text{K}_2\text{Fe}^{++}[\text{Fe}(\text{CN})_6] + \text{K}_2\text{SO}_4\text{Aq}$ Potassium Ferrous Ferrocyanide	5) Deep blue precipitate of Ferric Ferrocyanide — Prussian blue. $4\text{FeCl}_3\text{Aq} + 3\text{K}_4\text{Fe}(\text{CN})_6\text{Aq} = \text{Fe}_3[\text{Fe}(\text{CN})_6]_3 + 12\text{KClAq}$ Ferric Ferrocyanide	Distinction between Ferrous and Ferric Compounds.
6. K <sub>3</sub> Fe(CN) <sub>6</sub>	Deep blue precipitate of Ferrous Ferricyanide — Turnbull's blue. $3\text{FeSO}_4\text{Aq} + 2\text{K}_3\text{Fe}(\text{CN})_6\text{Aq} = \text{Fe}_3[\text{Fe}(\text{CN})_6]_2 + 3\text{K}_2\text{SO}_4\text{Aq}$ Ferrous Ferricyanide	6) Solution turns brown, but no precipitate is formed.	Distinction between Ferrous and Ferric Compounds.
7. KCNS	No precipitate and if absolutely pure no coloration. A trace of Ferric Salt is usually present, causing the solution to become tinted a light pink.	7) Deep red coloration or precipitate of Ferric Sulphocyanide. $\text{FeCl}_3\text{Aq} + 3\text{KSCNAq} = \text{Fe}(\text{SCN})_3 + 3\text{KClAq}$	
8. Reduction on Charcoal	A metallic residue is obtained, which is attracted by a magnet.		
9. Borax bead	Brownish bead in the oxidizing flame—bottle green in the reducing flame.		

**Summary regarding Iron and its notable Compounds,**  
most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
Fe	<b>Metallic Iron</b> , m. pt. about 1550° C.	Met with in different forms, e. g. filings, wire, sheet, &c.—grey metal.	Soluble in acids.	Reduction by C or CO.
<b>A. FERROUS COMPOUNDS.</b>				
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	<b>Ferrous Chloride</b>	Light green crystalline solid.	Soluble in water.	3
$\text{FeBr}_2$	<b>Ferrous Bromide</b>	do.	do.	Direct union.
$\text{FeI}_2$	<b>Ferrous Iodide</b>		do.	do.
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	<b>Ferrous Sulphate</b>	Green crystalline solid.	do.	3
$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	<b>Ferrous Ammonium Sulphate</b>	Light green crystalline solid.	do.	
$\text{Fe}_3(\text{PO}_4)_2$	<b>Ferrous Phosphate</b>	Bluish grey powder.	Insoluble in water; soluble in acids.	4
$\text{FeCO}_3$	<b>Ferrous Carbonate</b> (the ore is called <b>Spathic iron ore</b> )	Greyish white solid—the natural ore is grey.	Insoluble in water; soluble in acids with decomposition.	4
$\text{FeC}_2\text{O}_4$	<b>Ferrous Oxalate</b>	Yellow solid.	Insoluble in water; soluble in acids.	4
(FeO)	<b>Ferrous Oxide</b>	Black powder.	Soluble in acids.	Heat $\text{FeC}_2\text{O}_4$ .
FeS	<b>Ferrous Sulphide</b>	a) Black solid or b) Sticks with grey metallic lustre.	Soluble in $\text{HCl}$ aq. or $\text{H}_2\text{SO}_4$ aq. $\text{H}_2\text{S}$ being given off.	4 or direct union.
<b>B. FERRIC COMPOUNDS.</b>				
$\text{FeCl}_3$	<b>Ferric Chloride</b>	Pure anhydrous compound is black, but the hydrated body is yellow.	Soluble in water to give a yellow solution.	Direct union or 1.
$\text{Fe}(\text{NO}_3)_3$	<b>Ferric Nitrate</b>	Yellow cryst. solid.	do.	1
$\text{Fe}_2(\text{SO}_4)_3$	<b>Ferric Sulphate</b>	Nearly white solid.	do.	1 or oxidation of $\text{FeSO}_4$ .
$\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$	<b>Iron Alum</b>	Light violet solid.	Soluble in water to give a yellow solution.	
$\text{FePO}_4$	<b>Ferric Phosphate</b>	Faintly yellow solid—nearly white.	Soluble in acids.	4
$\text{Fe}_2(\text{CO}_3)_3 \cdot x\text{Fe}_2\text{O}_3$	<b>(Ferric Carbonate)</b>	Brown powder consisting chiefly of Oxide of Iron.	Soluble in acids.	4
$\text{Fe}(\text{OH})_3$	<b>Ferric Hydroxide</b>	Brown solid.	Easily soluble in acids.	4
$\text{Fe}_2\text{O}_3$	<b>Ferric Oxide</b>	Occurs in many forms, e. g. a) rust, b) hematite, c) specular iron ore.	Soluble in Hydrochloric Acid unless strongly ignited.	
$\text{Fe}_3\text{O}_4$	<b>Magnetic Oxide of iron</b> (Lodestone, Triferric Tetroxide)	Brown solid.	Soluble in acids with difficulty.	

Alloy :—Cast iron contains 93–94 % Fe, 3–4 % C; and also Si. P. S. (and Mn.).

Summary of Reactions for Chromium. Cr<sup>+++</sup>. 52.Use a solution of Chromium Sulphate, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, or Chrome Alum,

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	
2. H <sub>2</sub> S (in presence of HCl)	No precipitate.	
3. (NH <sub>4</sub> ) <sub>2</sub> S	A greyish green precipitate of Chromium Hydroxide, Cr(OH) <sub>3</sub> , is thrown down. $\text{Cr}_2(\text{SO}_4)_3\text{Aq} + 3(\text{NH}_4)_2\text{SAq} + 6\text{H}_2\text{O} \\ = 2\text{Cr}(\text{OH})_3 + 3(\text{NH}_4)_2\text{SO}_4\text{Aq} + 3\text{H}_2\text{S}$	Cr <sub>2</sub> S <sub>3</sub> is decomposed by water, which explains this reaction (cf. Al).
4. NH <sub>4</sub> OH, KOH, or NaOH	Greyish green precipitate of Chromium Hydroxide, Cr(OH) <sub>3</sub> . $\text{Cr}_2(\text{SO}_4)_3\text{Aq} + 6\text{NH}_4\text{OHAq} \\ = 2\text{Cr}(\text{OH})_3 + 3(\text{NH}_4)_2\text{SO}_4\text{Aq}$	
5. Bleaching powder and then (CH <sub>3</sub> COO) <sub>2</sub> Pb	The solution turns yellow because the Chromic salt is oxidized to a Chromate. Add to the solution Lead Acetate. A yellow precipitate of Lead Chromate is thrown down. a) $\text{Cr}_2(\text{SO}_4)_3\text{Aq} + 6\text{CaOCl}_2\text{Aq} + 3\text{H}_2\text{O} \\ = 2\text{H}_2\text{CrO}_4\text{Aq} + 6\text{CaCl}_2 + 3\text{H}_2\text{SO}_4\text{Aq}$ b) $\text{H}_2\text{CrO}_4\text{Aq} + (\text{CH}_3\text{COO})_2\text{PbAq} \\ = \text{PbCrO}_4 + 2\text{CH}_3\text{COOHAq}$	The Chromium is changed by oxidation from basic radicle to a portion of the acid radicle.
6. Heat the dry powder with Na <sub>2</sub> O <sub>2</sub> or KNO <sub>3</sub> in a hard glass tube	The mixture turns yellow because of the formation of a Chromate. Break the tube in a mortar, add water, filter, and add Lead Acetate to the solution. Lead Chromate is precipitated. a) $\text{Cr}_2(\text{SO}_4)_3 + 3\text{Na}_2\text{O}_2 = 3\text{Na}_2\text{SO}_4 + 2\text{CrO}_3$ b) $\text{CrO}_3 + \text{H}_2\text{O} = \text{H}_2\text{CrO}_4$ c) $\text{H}_2\text{CrO}_4\text{Aq} + (\text{CH}_3\text{COO})_2\text{PbAq} \\ = \text{PbCrO}_4 + 2\text{CH}_3\text{COOHAq}$	
7. Borax bead	Green.	

## Summary regarding Chromium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
(Cr	Metallic Chromium	Grey metal.	Soluble in HClAq.	Reduction by Al or C.)
<b>A. CHROMIC COMPOUNDS.</b>				
CrCl <sub>3</sub>	Chromium Trichloride	The hydrated substance is green, and the anhydrous compound violet.	The hydrated substance is easily soluble in water.	1 and direct union.
Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Chromium Sulphate	Green solid.	Soluble in water.	1
K <sub>2</sub> SO <sub>4</sub> · Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 24H <sub>2</sub> O or KCr(SO <sub>4</sub> ) <sub>2</sub> · 12H <sub>2</sub> O	Chrome Alum	Purple solid.	do.	
CrPO <sub>4</sub>	Chromium Phosphate	Green solid.	Insoluble in water; soluble in acids.	4
Cr <sub>2</sub> O <sub>3</sub>	Chromic Oxide	Bright green solid.	Soluble in concentrated Hydrochloric Acid unless the Oxide has been strongly ignited.	Heat the hydroxide.
Cr(OH) <sub>3</sub>	Chromium Hydroxide	Greyish green solid.	Soluble in acids.	
<b>B. CHROMIC ANHYDRIDE AND ITS DERIVATIVES.</b>				
CrO <sub>3</sub>	Chromium Trioxide Chromic Anhydride	Dark red solid.	Soluble in water to give a yellow solution of Chromic Acid. $\text{CrO}_3 + \text{H}_2\text{O} = \text{H}_2\text{CrO}_4$	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> and H <sub>2</sub> SO <sub>4</sub> .
K <sub>2</sub> CrO <sub>4</sub>	Potassium Chromate	Bright yellow solid. The solution is reduced by Sulphur Dioxide to give a green solution of Chromic Sulphate. SH <sub>2</sub> also reduces.	Soluble in water.	
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Potassium Dichromate	Deep orange solid. The solution is reduced by SO <sub>2</sub> or H <sub>2</sub> S.	Soluble in water.	
Ag <sub>2</sub> CrO <sub>4</sub>	Silver Chromate	Dark red solid.	Soluble in acids.	4
BaCrO <sub>4</sub>	Barium Chromate	Light yellow solid.	Soluble in mineral acids (i.e. HCl, H <sub>2</sub> SO <sub>4</sub> , or HNO <sub>3</sub> ); insoluble in Acetic Acid.	4
PbCrO <sub>4</sub>	Lead Chromate	Dark yellow solid.	Soluble in mineral acids unless strongly ignited.	4

### Group IV. Zn. Mn.

#### Summary of Reactions for Zinc. Zn. 65.

Use a solution of Zinc Sulphate or Zinc Chloride.

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	
2. H <sub>2</sub> S (in presence of HCl)	No precipitate.	
3. (NH <sub>4</sub> ) <sub>2</sub> S	<b>White precipitate of Zinc Sulphide, ZnS.</b> $\text{ZnSO}_4\text{Aq} + (\text{NH}_4)_2\text{SAq} = \text{ZnS} + (\text{NH}_4)_2\text{SO}_4\text{Aq}$	
4. NH <sub>4</sub> OH	<b>White precipitate of Zinc Hydroxide, Zn(OH)<sub>2</sub>,</b> soluble in Ammonium Chloride, NH <sub>4</sub> Cl. $\text{ZnSO}_4\text{Aq} + 2\text{NH}_4\text{OHAq} = \text{Zn(OH)}_2 + (\text{NH}_4)_2\text{SO}_4\text{Aq}$	
5. KOH or NaOH	<b>White precipitate of Zinc Hydroxide, soluble</b> in excess of reagent, forming a zincate. a) $\text{ZnSO}_4\text{Aq} + 2\text{KOHAg} = \text{Zn(OH)}_2 + \text{K}_2\text{SO}_4\text{Aq}$ b) $\text{Zn(OH)}_2 + 2\text{KOHAg} = \text{Zn(OK)}_2\text{Aq} + 2\text{H}_2\text{O}$	Cf. Al.
6. K <sub>3</sub> Fe(CN) <sub>6</sub>	<b>Orange precipitate of Zinc Ferricyanide.</b> $3\text{ZnSO}_4\text{Aq} + 2\text{K}_3\text{Fe(CN)}_6\text{Aq} = \text{Zn}_3[\text{Fe(CN)}_6]_2 + 3\text{K}_2\text{SO}_4\text{Aq}$ Potassium Ferricyanide Zinc Ferricyanide	
7. K <sub>4</sub> Fe(CN) <sub>6</sub>	<b>White precipitate of Zinc Ferrocyanide.</b> $2\text{ZnSO}_4\text{Aq} + \text{K}_4\text{Fe(CN)}_6\text{Aq} = \text{Zn}_2[\text{Fe(Cn)}_6] + 2\text{K}_2\text{SO}_4\text{Aq}$	
8. Co(NO <sub>3</sub> ) <sub>2</sub>	Moisten a few square centimetres of filter paper with a concentrated solution of the substance and then with a solution of Cobalt Nitrate. After ignition in Bunsen flame a <b>green residue</b> is left. Or, Heat on Charcoal, moisten with Cobalt Nitrate, and reheat.—Yellowish green mass is obtained.	
9. Ignition	The Oxide is white when cold, but turns yellow on heating, and white again on cooling.	



**Summary regarding Zinc and its notable Compounds,**  
most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
<b>Zn</b>	<b>Metallic Zinc,</b> m. pt. 430° C.	Silvery metal. Met with in many forms, e.g. stick, granulated, foil, and as a bluish grey powder.	Soluble in acids.	Reduction by Carbon.
<b>ZnCl<sub>2</sub></b>	<b>Zinc Chloride</b>	White solid—anhydrous compound is deliquescent and caustic.	Soluble in water.	1. 2. 3
<b>ZnBr<sub>2</sub></b>	<b>Zinc Bromide</b>	White solid.	do.	1. 2
<b>ZnI<sub>2</sub></b>	<b>Zinc Iodide</b>	White solid.	do.	1. 2
<b>Zn(NO<sub>3</sub>)<sub>2</sub></b>	<b>Zinc Nitrate</b>	do.	do.	1. 2. 3
<b>ZnSO<sub>4</sub> . 7H<sub>2</sub>O</b>	<b>Zinc Sulphate</b>	do.	do.	1. 2. 3
<b>ZnCO<sub>3</sub></b>	<b>Zinc Carbonate</b> (natural substance is called Calamine)	do.	Soluble in acids with decomposition.	4
<b>Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub></b>	<b>Zinc Phosphate</b>	do.	Soluble in acids.	4
<b>ZnO</b>	<b>Zinc Oxide</b> (Zinc white)	do. Turns yellow on heating, and white again on cooling.	do.	Heat metal or Carbonate.
<b>ZnS</b>	<b>Zinc Sulphide</b> (natural substance is called Blende)	White solid.	Soluble in HCl. H <sub>2</sub> S is evolved.	4

Alloys :—Brass, 20-40 % Zn. Cu.  
Bronze, Cu. Zn. Sn. Pb.  
German Silver, Cu. Zn. Ni.

### Summary of Reactions for Manganese. $Mn^{++}$ . 55.

Use a solution of Manganous Sulphate ( $MnSO_4$ ) or Chloride ( $MnCl_2$ ).

Reagent.	Results observed.	Remarks.
1. $HCl$	No precipitate.	
2. $H_2S$ (in presence of $HCl$ )	No precipitate.	
3. $(NH_4)_2S$	Salmon pink precipitate of Manganous Sulphide ( $MnS$ ). $MnSO_4Aq + (NH_4)_2SAq = MnS + (NH_4)_2SO_4Aq$	
4. $NH_4OH$ , $KOH$ , or $NaOH$	White precipitate of Manganous Hydroxide, $Mn(OH)_2$ , which rapidly turns brown on shaking with air, owing to formation of Manganic Hydroxide, $Mn(OH)_3$ . a) $MnSO_4Aq + 2NH_4OHAq = \underset{\substack{\text{Manganous} \\ \text{Hydroxide.}}}{Mn(OH)_2} + (NH_4)_2SO_4Aq$ b) $2Mn(OH)_2 + H_2O + O = \underset{\substack{\text{from} \\ \text{air}}}{2Mn(OH)_3}$ Manganic Hydroxide.	No precipitate is obtained on adding $NH_4OH$ to a manganous salt if a sufficiency of Ammonium Chloride be present.
5. Bleaching powder	A brown precipitate of the hydrated Peroxide of Manganese— $MnO_2 \cdot xH_2O$ —is obtained. $MnSO_4Aq + CaOCl_2^* + Ca(OH)_2^* = MnO_2 + CaCl_2Aq + CaSO_4Aq + H_2O$	* Bleaching powder is chiefly a mixture of $CaOCl_2$ and $Ca(OH)_2$ . In solution it behaves as if it were a mixture of $Ca(OCl)_2$ , $CaCl_2$ , and $Ca(OH)_2$ .
6. $Na_2O_2$ or $KNO_3$	On heating the dry ignited powdered substance in a tube with Sodium Peroxide or Potassium Nitrate, the Manganese Compound is oxidized to greenish Manganate, $K_2MnO_4$ , which dissolves in water, giving first a green tint, which changes to pink on dilution owing to conversion to Permanganate, $KMnO_4$ .	
7. Borax bead	Amethyst-coloured bead is obtained.	

## Summary regarding Manganese and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
Mn	Metallic Manganese	Greyish metal.	Soluble in acids.	Reduction by C or Al.
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	Manganous Chloride	Light pink solid.	Soluble in water.	1. 2
$\text{Mn}(\text{NO}_3)_2$	Manganous Nitrate	do.	do.	1. 2
$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	Manganous Sulphate	do.	do.	1. 2
$\text{MnCO}_3$	Manganous Carbonate	Nearly white powder (slowly turns brown in air).	Soluble in acids with decomposition.	
$\text{Mn}_3(\text{PO}_4)_2$	Manganous Phosphate	Nearly white solid.	Soluble in acids.	
(MnO	Manganous Oxide	Greenish powder.	do.)	
$\text{Mn}_2\text{O}_3$	Occurs native Braunite	Brownish solid.	Soluble in acids.	
$\text{Mn}_3\text{O}_4$	Occurs native Hausmannite	Black solid.	do.	Decomposition of $\text{MnO}_2$ by heat.
$\text{MnO}_2$	Manganese Peroxide (Natural substance is called Pyrolusite).	Black powder, granules, or lumps.	Soluble in $\text{HClAq}$ on warming to give $\text{MnCl}_2$ and Chlorine.	
$\text{Na}_2\text{MnO}_4$	Sodium Manganate	Green solid.	Soluble in water to give green solutions, which turn pink on dilution owing to conversion to Permanganate.	
$\text{K}_2\text{MnO}_4$		do.		
$\text{KMnO}_4$	Potassium Permanganate	Dark purple solid.	Soluble in water to give a purple solution.	
$\text{NaMnO}_4$	Sodium Permanganate	do.	do.	

# Summary of Reactions for Barium. Ba<sup>++</sup>. 137.

Use a solution of Barium Nitrate or Chloride.

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	Conc. HClAq precipitates BaCl <sub>2</sub> from strong solutions.
2. H <sub>2</sub> S (in presence of HCl)	No precipitate.	
3. NH <sub>4</sub> OH, KOH, or NaOH	White precipitate of Barium Hydroxide may form in concentrated solution, but not if Ammonium Chloride be present. $\text{BaCl}_2\text{Aq} + 2\text{NH}_4\text{OHAq} = \text{Ba}(\text{OH})_2 + 2\text{NH}_4\text{ClAq}$	
(4. (NH <sub>4</sub> ) <sub>2</sub> S	White precipitate of Barium Hydroxide might be obtained from very conc. solutions, but not if Ammonium Chloride be present.	Omit as a test.)
5. (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	White precipitate of Barium Carbonate is formed. $\text{BaCl}_2\text{Aq} + (\text{NH}_4)_2\text{CO}_3\text{Aq} = \text{BaCO}_3 + 2\text{NH}_4\text{ClAq}$	
6. K <sub>2</sub> CrO <sub>4</sub>	Yellow precipitate of Barium Chromate (BaCrO <sub>4</sub> ) is obtained, insoluble in Acetic Acid. $\text{BaCl}_2\text{Aq} + \text{K}_2\text{CrO}_4\text{Aq} = \text{BaCrO}_4 + 2\text{KClAq}$	Distinction from Strontium and Calcium.
7. CaSO <sub>4</sub>	Immediate white precipitate of Barium Sulphate (BaSO <sub>4</sub> ). $\text{BaCl}_2\text{Aq} + \text{CaSO}_4\text{Aq} = \text{BaSO}_4 + \text{CaCl}_2\text{Aq}$	Compare Strontium.
8. H <sub>2</sub> SO <sub>4</sub>	White precipitate of Barium Sulphate. $\text{Ba}(\text{NO}_3)_2\text{Aq} + \text{H}_2\text{SO}_4\text{Aq} = \text{BaSO}_4 + 2\text{HNO}_3\text{Aq}$	
9. (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	White precipitate of Barium Oxalate. $\text{BaCl}_2\text{Aq} + (\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq} = \text{BaC}_2\text{O}_4 + 2\text{NH}_4\text{ClAq}$	
10. Platinum wire test	Apple green flame.	On heating a Barium Compound on Platinum wire use concentrated HCl, and note remark on p. 88.

**Summary regarding Barium and its notable Compounds,**  
most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
(Ba	Metallic Barium	Greyish white metal.	Reacts with water to form $\text{Ba}(\text{OH})_2$ and Hydrogen.)	Electrolysis of fused Chloride.
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	Barium Chloride	White crystalline solid.	Soluble in water.	1. 2
$\text{BaBr}_2$	Barium Bromide	do.	do.	1. 2
$\text{BaI}_2$	Barium Iodide	do.	do.	1. 2
$\text{Ba}(\text{NO}_3)_2$	Barium Nitrate	do.	do.	1. 2
$\text{BaCO}_3$	Barium Carbonate (native subs. is called Witherite)	White powder (or native subs. in lumps).	Soluble in acids.	4
$\text{BaSO}_4$	Barium Sulphate (native subs. is called Heavy spar or Barytes)	White powder or massive.	Insoluble in water and acids. To get into solution two methods can be used : a) Fuse up with $\text{Na}_2\text{CO}_3$ . $\text{BaSO}_4 + \text{Na}_2\text{CO}_3 = \text{BaCO}_3 + \text{Na}_2\text{SO}_4$ b) Heat up with Carbon. $\text{BaSO}_4 + 4\text{C} = \text{BaS} + 4\text{CO}$	4
$\text{BaSO}_3$	Barium Sulphite	White solid.	Soluble in acids with decomposition.	4
$\text{Ba}_3(\text{PO}_4)_2$	Barium Phosphate	do.	Soluble in acids.	4
$\text{BaC}_2\text{O}_4$	Barium Oxalate	do.	do.	4
$\text{BaCrO}_4$	Barium Chromate	Yellow solid.	Soluble in $\text{HCl}$ or $\text{HNO}_3$ but not in Acetic Acid.	4
$\text{BaO}$	Barium Oxide	Nearly white solid.	Reacts with water to form the hydroxide. $\text{BaO} + \text{H}_2\text{O} = \text{Ba}(\text{OH})_2$	Heat the Nitrate.
$\text{Ba}(\text{OH})_2$	Barium Hydroxide (Baryta)	White solid.	Soluble in water.	Oxide and water.
$\text{BaO}_2$	Barium Peroxide	do.	do.	Heat Oxide in air.
$\text{BaS}$	Barium Sulphide	do.	Nearly insol. in water, but slowly undergoes hydrolysis, forming $\text{Ba}(\text{OH})_2$ and $\text{Ba}(\text{SH})_2$ —soluble in acids with decomposition.	$\text{BaSO}_4$ and C.

### Summary of Reactions for Strontium. Sr<sup>++</sup>. 87.

Use a solution of Strontium Chloride or Nitrate.

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	
2. H <sub>2</sub> S (in presence of HCl)	No precipitate.	
3. NH <sub>4</sub> OH, KOH, or NaOH	A white precipitate of Strontium Hydroxide, Sr(OH) <sub>2</sub> , might form from a concentrated solution, but not in presence of excess of Ammonium Chloride. $\text{SrCl}_2\text{Aq} + 2\text{NH}_4\text{OHAq} = \text{Sr(OH)}_2 + 2\text{NH}_4\text{Cl}$	Of no value as a test.
4. (NH <sub>4</sub> ) <sub>2</sub> S	No precipitate.	
5. (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	White precipitate of Strontium Carbonate, SrCO <sub>3</sub> . $\text{SrCl}_2\text{Aq} + (\text{NH}_4)_2\text{CO}_3\text{Aq} = \text{SrCO}_3 + 2\text{NH}_4\text{ClAq}$	
6. CaSO <sub>4</sub>	White precipitate of Strontium Sulphate, SrSO <sub>4</sub> , forms slowly. $\text{SrCl}_2\text{Aq} + \text{CaSO}_4\text{Aq} = \text{SrSO}_4 + \text{CaCl}_2\text{Aq}$	Allow to stand ten minutes if necessary.
7. H <sub>2</sub> SO <sub>4</sub>	White precipitate of Strontium Sulphate, SrSO <sub>4</sub> (slowly from dilute solutions). $\text{SrCl}_2\text{Aq} + \text{H}_2\text{SO}_4\text{Aq} = \text{SrSO}_4 + 2\text{HClAq}$	
8. K <sub>2</sub> CrO <sub>4</sub>	As a rule no precipitate is obtained, but a yellow precipitate may form from very concentrated solutions, easily soluble in Acetic Acid. $\text{SrCl}_2\text{Aq} + \text{K}_2\text{CrO}_4\text{Aq} = \text{SrCrO}_4 + 2\text{KClAq}$	Distinction from Barium.
9. (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	White precipitate of Strontium Oxalate, SrC <sub>2</sub> O <sub>4</sub> . $\text{SrCl}_2\text{Aq} + (\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq} = \text{SrC}_2\text{O}_4 + 2\text{NH}_4\text{ClAq}$	
10. Platinum wire test	Crimson flame.	Calcium gives a less brilliant, and Lithium a deeper red flame. Characteristic lines in spectra.

## Summary regarding Strontium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
(Sr	Metallic Strontium	Not met with.)		
$\text{SrCl}_2$	Strontium Chloride	White solid.	Soluble in water.	1. 2
$\text{SrBr}_2$	Strontium Bromide	do.	do.	1. 2
$\text{SrI}_2$	Strontium Iodide	do.	do.	1. 2
$\text{Sr}(\text{NO}_3)_2$	Strontium Nitrate	do.	do.	1. 2
$\text{SrCO}_3$	Strontium Carbonate (native substance is called Strontianite)	do.	Soluble in acids with decomposition.	4
$\text{SrSO}_4$	Strontium Sulphate (native substance is called Celestine)	do.	Slightly soluble in water (1 part in 7,000).	4
$\text{Sr}_3(\text{PO}_4)_2$	Strontium Phosphate	do.	Soluble in acids.	4
$(\text{SrCrO}_4$	Strontium Chromate	Yellow solid.	Sparingly soluble in water.	1. 4)
$\text{SrO}$	Strontium Oxide	White solid.	Reacts with water to form the hydroxide.	Heat the Carbonate.
$\text{Sr}(\text{OH})_2$	Strontium Hydroxide	do.	Sparingly soluble in water—solution is strongly alkaline in reaction.	Heat the Carbonate in super-heated steam.

### Summary of Reactions for Calcium. Ca<sup>++</sup>. 40.

Use a solution of Calcium Chloride (CaCl<sub>2</sub>) or Nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>).

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	
2. H <sub>2</sub> S (in presence of HCl)	No precipitate.	
3. (NH <sub>4</sub> ) <sub>2</sub> S	No precipitate.	
4. NH <sub>4</sub> OH, KOH, or NaOH	A white precipitate of Calcium Hydroxide, Ca(OH) <sub>2</sub> , may form from concentrated solutions, but not in presence of excess of Ammonium Chloride. CaCl <sub>2</sub> Aq + 2NH <sub>4</sub> OHAq = Ca(OH) <sub>2</sub> + 2NH <sub>4</sub> ClAq	
5. (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	White precipitate of Calcium Carbonate, CaCO <sub>3</sub> . CaCl <sub>2</sub> Aq + (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> Aq = CaCO <sub>3</sub> + 2NH <sub>4</sub> ClAq	
6. CaSO <sub>4</sub>	No precipitate.	Distinction from Barium and Strontium.
7. H <sub>2</sub> SO <sub>4</sub>	A white precipitate may form depending upon the concentration of the solution. CaCl <sub>2</sub> Aq + H <sub>2</sub> SO <sub>4</sub> Aq = CaSO <sub>4</sub> + 2HClAq	
8. K <sub>2</sub> CrO <sub>4</sub>	A slight yellow precipitate may form from concentrated solutions which is easily soluble in Acetic Acid. CaCl <sub>2</sub> Aq + K <sub>2</sub> CrO <sub>4</sub> Aq = CaCrO <sub>4</sub> + 2KClAq	Distinction from Barium.
9. (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	White precipitate of Calcium Oxalate, CaC <sub>2</sub> O <sub>4</sub> , insoluble in Acetic Acid. CaCl <sub>2</sub> Aq + (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> Aq = CaC <sub>2</sub> O <sub>4</sub> + 2NH <sub>4</sub> ClAq	
10. Platinum wire test	On moistening the substance with concentrated Hydrochloric Acid, and heating on Platinum wire in the oxidizing flame— <b>Brick red</b> flame.	The flame is less brilliant than that of Strontium or Lithium.



# Summary regarding Calcium and its notable Compounds, most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
Ca	<b>Metallic Calcium</b>	Grey solid.	Reacts with water to give Hydrogen and $\text{Ca(OH)}_2$ . $\text{Ca} + 2\text{HOH} = \text{Ca(OH)}_2 + \text{H}_2$	Electrolysis of $\text{CaCl}_2$ .
$\text{CaCl}_2$	<b>Calcium Chloride</b>	Met with generally as a granular solid, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ —also in lumps and in crystals.	Very soluble in water.	1. 2
$\text{CaBr}_2$	Calcium Bromide	White solid.	Soluble in water.	1. 2
$\text{CaI}_2$	Calcium Iodide	do.	do.	1. 2
$\text{Ca(NO}_3)_2$	<b>Calcium Nitrate</b>	do.	do.	1. 2
$\text{CaCO}_3$	<b>Calcium Carbonate (Marble, Limestone, Calc-spar)</b>	Met with in many forms — Limestone, Coral, Marble, Calc-spar, Chalk.	Soluble in acids with decomposition.	4
$\text{CaSO}_4$	<b>Calcium Sulphate (Gypsum, Selenite Anhydrite, Plaster of Paris)</b>	Occurs in various forms, generally as a white solid. Gypsum and Selenite have the composition $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .	Slightly soluble in water —about 1 part in 500.	4
$\text{CaSO}_3$	Calcium Sulphite	White solid.	Soluble in acids.	4
$\text{Ca}_3(\text{PO}_4)_2$	<b>Calcium Phosphate</b>	do.	do.	4
$\text{Ca} \cdot \text{C}_2\text{O}_4$	<b>Calcium Oxalate</b>	do.	do.	4
$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ or $(\text{CH}_3\text{COO})_2\text{Ca}$	<b>Calcium Acetate</b>	do.	Soluble in water.	1. 2
$\text{Ca} \cdot \text{C}_4\text{H}_4\text{O}_6$	<b>Calcium Tartrate</b>	do.	Soluble in acids.	4
$\text{CaCrO}_4$	Calcium Chromate	Light yellow solid.	Soluble in water.	1. 2
<b>CaO</b>	<b>Calcium Oxide (Quicklime)</b>	White solid if pure.	<b>Reacts vigorously with water to form slaked lime, Calcium Hydroxide.</b> $\text{CaO} + \text{H}_2\text{O} = \text{Ca(OH)}_2$ .	Heat $\text{CaCO}_3$ .
$\text{Ca(OH)}_2$	<b>Calcium Hydroxide (Slaked Lime)</b>	White solid if pure.	Soluble in water to give 'Lime-water'.	Water and $\text{CaO}$ .
$\text{CaO}_2$	Calcium Peroxide	White solid.		
<b>CaS</b>	<b>Calcium Sulphide</b>	do.	Nearly insoluble in water, but undergoes hydrolysis to give $\text{Ca(OH)}_2$ and $\text{Ca(SH)}_2$ . Soluble in acids, giving off $\text{H}_2\text{S}$ .	$\text{CaSO}_4$ and C.
$(\text{CaF}_2)$	Calcium Fluoride (Fluor-spar).	Whitesolid, but natural subs. is often in transparent crystals tinted by metallic oxides.	Soluble in acids, often with difficulty.	4)

**Summary of Reactions for Magnesium. Mg<sup>++</sup>. 24.**

Use a solution of **Magnesium Sulphate (MgSO<sub>4</sub>)** or **Magnesium Chloride (MgCl<sub>2</sub>)**.

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	
2. H <sub>2</sub> S (in presence of HCl)	No precipitate.	
3. NH <sub>4</sub> OH, KOH, or NaOH	$\left. \begin{array}{l} \text{White precipitate of Magnesium Hydroxide,} \\ \text{Mg(OH)}_2, \text{ which dissolves on addition of Am-} \\ \text{monium Chloride, NH}_4\text{Cl.} \end{array} \right\}$ e. g. $\text{MgSO}_4\text{Aq} + 2\text{NH}_4\text{OHAq}$ $\quad\quad\quad = \text{Mg(OH)}_2 + (\text{NH}_4)_2\text{SO}_4\text{Aq}$	
4. (NH <sub>4</sub> ) <sub>2</sub> S	No precipitate.	
5. (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	White precipitate of Magnesium Carbonate (MgCO <sub>3</sub> ) may form, which dissolves in Ammonium Chloride solution. e. g. $\text{MgSO}_4\text{Aq} + (\text{NH}_4)_2\text{CO}_3\text{Aq}$ $\quad\quad\quad = \text{MgCO}_3 + (\text{NH}_4)_2\text{SO}_4\text{Aq}$	
(6. Na <sub>2</sub> HPO <sub>4</sub>	White precipitate of Magnesium Phosphate (MgHPO <sub>4</sub> or Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ), the exact constitution of which depends upon the conditions of the experiment. $\text{MgSO}_4\text{Aq} + \text{Na}_2\text{HPO}_4\text{Aq} = \text{MgHPO}_4 + \text{Na}_2\text{SO}_4\text{Aq}$	
7. Na <sub>2</sub> HPO <sub>4</sub> and NH <sub>4</sub> OH	White precipitate of Magnesium, Ammonium Phosphate. $\text{MgSO}_4\text{Aq} + \text{NH}_4\text{OHAq} + \text{Na}_2\text{HPO}_4\text{Aq}$ $\quad\quad\quad = \text{MgNH}_4\text{PO}_4 + \text{Na}_2\text{SO}_4\text{Aq}$	Group test for Magnesium (see pp. 164 and 166).
8. Co(NO <sub>3</sub> ) <sub>2</sub>	Moisten a few square centimetres of filter paper with the concentrated solution, pour over the same area a solution of Cobalt Nitrate, and then burn in oxidizing flame. <b>Pink residue.</b>	

## Summary regarding Magnesium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
<b>Mg</b>	<b>Metallic Magnesium</b>	Silvery white metal. Met with as foil, powder, ribbon, wire.	Soluble in acids.	Electrolysis of Chloride.
<b>MgCl<sub>2</sub></b>	<b>Magnesium Chloride</b>	White solid.	Soluble in water.	1. 2. 3
<b>MgBr<sub>2</sub></b>	<b>Magnesium Bromide</b>	do.	do.	1. 2
<b>MgI<sub>2</sub></b>	<b>Magnesium Iodide</b>	do.	do.	1. 2
<b>Mg(NO<sub>3</sub>)<sub>2</sub></b>	<b>Magnesium Nitrate</b>	do.	do.	1. 2
<b>MgSO<sub>4</sub> . 7H<sub>2</sub>O</b>	<b>Magnesium Sulphate</b>	do.	do.	1. 2. 3
<b>MgCO<sub>3</sub></b>	<b>Magnesium Carbonate</b> (Natural subs. is called <b>Magnesite</b> . The double compound, MgCa(CO <sub>3</sub> ) <sub>2</sub> , is called <b>Dolomite</b> )	do.	Soluble in acids with decomposition, CO <sub>2</sub> being evolved.	4
<b>Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub></b>	<b>Magnesium Phosphate</b>	do.	Soluble in acids.	4
<b>MgC<sub>2</sub>O<sub>4</sub></b>	<b>Magnesium Oxalate</b>	do.	do.	4
<b>Mg(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub></b> or <b>(CH<sub>3</sub>COO)<sub>2</sub>Mg</b>	<b>Magnesium Acetate</b>	do.	Soluble in water.	1. 2
<b>MgO</b>	<b>Magnesium Oxide</b> ( <b>Magnesia</b> )	do. Glows with white light on heating strongly.	Soluble in acids.	Heat the Carbonate.
<b>Mg(OH)<sub>2</sub></b>	<b>Magnesium Hydroxide</b>	White solid.	Very slightly soluble in water; soluble in acids.	4
<b>Mg(NH<sub>4</sub>)PO<sub>4</sub></b>	<b>Magnesium Ammonium Phosphate</b>	do.	Very slightly soluble in water; less soluble in weak Ammonia.	4

### Summary of Reactions for the Radicle $\text{NH}_4$ .

Use a solution of **Ammonium Chloride** ( $\text{NH}_4\text{Cl}$ ), **Ammonium Sulphate** ( $(\text{NH}_4)_2\text{SO}_4$ ), or **Ammonium Nitrate** ( $\text{NH}_4\text{NO}_3$ ).

Reagent.	Results observed.	Remarks.
1. $\text{HCl}$	No precipitate.	
2. $\text{H}_2\text{S}$ (in presence of $\text{HCl}$ )	do.	
3. $\text{NH}_4\text{OH}$	do.	
4. $(\text{NH}_4)_2\text{CO}_3$	do.	
5. $\text{Na}_2\text{HPO}_4$	do.	
6. $\text{KOH}$ or $\text{NaOH}$	On boiling an Ammonium Compound with Potassium or Sodium Hydroxide, Ammonia is evolved. $\text{NH}_4\text{ClAq} + \text{KOH Aq} = \text{NH}_3 + \text{KCl Aq} + \text{H}_2\text{O}$	The odour of the evolved gas is characteristic, and the alkaline reaction towards moist red litmus paper.
7. $\text{NaHC}_4\text{H}_4\text{O}_6$ or $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	With concentrated solutions of Ammonium Salts, Sodium Hydrogen Tartrate or Tartaric Acid gives a white precipitate of Ammonium Hydrogen Tartrate, $\text{NH}_4 \cdot \text{H} \cdot \text{C}_4\text{H}_4\text{O}_6$ . $\text{NH}_4\text{Cl Aq} + \text{H}_2\text{C}_4\text{H}_4\text{O}_6\text{Aq} = \text{NH}_4 \cdot \text{HC}_4\text{H}_4\text{O}_6 + \text{HCl Aq}$	The test is rarely carried out, and is quite unnecessary, as Test 6 is conclusive. It must be kept in view to prevent mistake in the case of Potassium (p. 134).
8. $\text{H}_2\text{PtCl}_6$	Yellow precipitate of Ammonium Chloroplatinate, $(\text{NH}_4)_2\text{PtCl}_6$ . $\text{H}_2\text{PtCl}_6\text{Aq} + 2\text{NH}_4\text{Cl Aq} = (\text{NH}_4)_2\text{PtCl}_6 + 2\text{HCl Aq}$	Chloroplatinic Acid is too expensive for general use. Potassium Salts give a similar precipitate (p. 134).
9. Nessler's Reagent (alkaline solution of $\text{HgI}_2$ in $\text{KIAq}$ )	Brown precipitate of Dimercuric Ammonium Iodide, soluble in excess of Ammonium Salt. $\text{NH}_4\text{Cl Aq} + 2[\text{HgI}_2 \cdot 2\text{KI}] \text{Aq} + 4\text{KOH Aq} = \text{NH}_2\text{Hg}_2\text{I} \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O} + 7\text{KIAq} + \text{KCl Aq}$	This test is very delicate and will detect mere traces of Ammonium Salt (or Ammonia).

## Summary regarding Ammonium ( $\text{NH}_4^+$ ) and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
$\text{NH}_4$ The group $\text{NH}_4-$ is not met with : if set free it splits up into $\text{NH}_3$ and Hydrogen.				
$\text{NH}_4\text{Cl}$	Ammonium Chloride Sal Ammoniac	White solid.	Soluble in water.	
$\text{NH}_4\text{Br}$	Ammonium Bromide	do.	do.	1. 2
$\text{NH}_4\text{I}$	Ammonium Iodide	do.	do.	1. 2
$\text{NH}_4\text{NO}_3$	Ammonium Nitrate	do.	do.	1. 2
$\text{NH}_4\text{HSO}_4$	Ammonium Hydrogen Sulphate	do.	do.	1. 2
$(\text{NH}_4)_2\text{SO}_4$	Ammonium Sulphate	do.	do.	1. 2
$(\text{NH}_4)_2\text{SO}_3$	Ammonium Sulphite	do.	do.	
$(\text{NH}_4)_2\text{CO}_3$	Ammonium Carbonate	do.	do.	
$(\text{NH}_4)_2\text{HPO}_4$	Diammonium Hydrogen Phosphate	do.	do.	
$(\text{NH}_4)_2\text{CrO}_4$	Ammonium Chromate	Yellow solid.	do.	1. 2
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	Ammonium Dichromate	Orange.	do.	1. 2
$[(\text{NH}_4)_2\text{O}]$	Ammonium Oxide	Does not exist.	Splits into $\text{NH}_3$ and $\text{H}_2\text{O}$ at ordinary temp.]	
$\text{NH}_4\text{OH}$	Ammonium Hydroxide	Met with as a solution in water.	Solution in water smells of Ammonia.	$\text{NH}_3$ and $\text{H}_2\text{O}$ .
$(\text{NH}_4)_2\text{S}$	Ammonium Sulphide	White solid.	Soluble in water. Colourless solution.	$\text{NH}_3$ and $\text{H}_2\text{S}$ .
$(\text{NH}_4)_2\text{S}_x$	Ammonium Polysulphide	Yellow solid.	Soluble in water. Yellow solution.	
$\text{NH}_4\text{HC}_2\text{O}_4$	Ammonium Hydrogen Oxalate	White solid.	Soluble in water.	1. 2
$(\text{NH}_4)_2\text{C}_2\text{O}_4$	Ammonium Oxalate	do.	do.	1. 2
$\text{CH}_3\cdot\text{COONH}_4$	Ammonium Acetate	do.	do.	1. 2
$\text{NH}_4\text{H}\cdot\text{C}_4\text{H}_4\text{O}_6$	Ammonium Hyd. Tartrate	do.	Sparingly soluble in water.	4
$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$	Ammonium Tartrate	do.	Soluble in water.	1. 2

### Summary of Reactions for Potassium. K. 39.

Use a solution of Potassium Nitrate ( $\text{KNO}_3$ ), Chloride ( $\text{KCl}$ ), or Sulphate ( $\text{K}_2\text{SO}_4$ ).

Reagent.	Results observed.	Remarks.
1. $\text{HCl}$	No precipitate.	
2. $\text{H}_2\text{S}$ (in presence of $\text{HCl}$ )	do.	
3. $\text{NH}_4\text{OH}$	do.	
4. $(\text{NH}_4)_2\text{S}$	do.	
5. $(\text{NH}_4)_2\text{CO}_3$	do.	
6. $\text{Na}_2\text{HPO}_4$	do.	
7. $\text{NaHC}_4\text{H}_4\text{O}_6$ or $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	Sodium Hydrogen Tartrate or Tartaric Acid gives a <b>white precipitate</b> of <b>Potassium Hydrogen Tartrate</b> on addition to a concentrated solution of a Potassium Salt. $\text{KClAq} + \text{NaHC}_4\text{H}_4\text{O}_6\text{Aq} = \text{KH} \cdot \text{C}_4\text{H}_4\text{O}_6 + \text{NaClAq}$	If the precipitate does not form on shaking the tube, scratch the tube inside the liquid with a glass rod. The solution of Potassium Salt should be as concentrated as possible.
8. $\text{H}_2\text{PtCl}_6$	Chloroplatinic Acid, $\text{H}_2\text{PtCl}_6$ , gives a <b>yellow crystalline precipitate</b> of <b>Potassium Chloroplatinate</b> , $\text{K}_2\text{PtCl}_6$ , on addition to a concentrated solution of a Potassium Salt. $2\text{KNO}_3 + \text{H}_2\text{PtCl}_6\text{Aq} = \text{K}_2\text{PtCl}_6 + 2\text{HNO}_3\text{Aq}$	(cf. $\text{NH}_4$ ).
9. Platinum wire test	Violet flame.	Notes. a) <b>Pb, As, Sb, and Bi</b> all give blue flames which might be mistaken for the violet flame of Potassium. b) <b>Traces of Sodium</b> are frequently present and may mask the <b>Potassium flame</b> . Use a blue glass or a potassioscope.

**Summary regarding Potassium and its notable Compounds,**  
most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of pre-paration.
K	Metallic Potassium, m. pt. 53° C.	Bluishwhite lustre —easily tarnish- ed. Kept under petroleum oil.	Reacts with water. $2K + 2HOH$ $\quad \quad \quad = 2KOH + H_2$	Electro- lysis of KCl, &c.
KCl	Potassium Chloride	White cryst. solid.	Soluble in water.	1. 2
KBr	Potassium Bromide	do.	do.	KOH and Br <sub>2</sub> .
KI	Potassium Iodide	do.	do.	KOH and I <sub>2</sub> .
KNO <sub>3</sub>	Potassium Nitrate	do.	do.	1. 2
KNO <sub>2</sub>	Potassium Nitrite	Nearly white solid. Generally faint yellow tint.	do.	KNO <sub>3</sub> and Pb.
KHSO <sub>4</sub>	Potassium Hyd. Sulphate	White solid—acid reaction.	do.	1
K <sub>2</sub> SO <sub>4</sub>	Potassium Sulphate	White solid.	do.	1. 2
K <sub>2</sub> SO <sub>3</sub>	Potassium Sulphite	do.	do.	1
KHCO <sub>3</sub>	Potassium Hyd. Carbonate	do.	do.	1
K <sub>2</sub> CO <sub>3</sub>	Potassium Carbonate	do.	do.	1, &c.
K <sub>2</sub> HPO <sub>4</sub>	Dipotassium Hyd. Phosphate	do.	do.	1
K <sub>2</sub> CrO <sub>4</sub>	Potassium Chromate	Bright yellow solid.	do.	1
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Potassium Dichro- mate	Deep orange solid.	do.	1
(K <sub>2</sub> O	Potassium Oxide)	Nearly white solid.	Reacts with water to give Caustic Potash, KOH.	KNO <sub>3</sub> and K.
KOH	Potassium Hydroxide (Caustic Potash)	White deliques- cent solid—soapy feel, caustic.	Soluble in water— strongly alkaline re- action.	K <sub>2</sub> CO <sub>3</sub> and Ca(OH) <sub>2</sub> .
K <sub>2</sub> S	Potassium Sulphide	White solid.	Soluble in water.	1
K <sub>2</sub> S <sub>4</sub>	Potassium Polysulphide	Yellow solid.	Sol. in water. Yellow solution.	K <sub>2</sub> CO <sub>3</sub> and S.
KHC <sub>2</sub> O <sub>4</sub>	Potassium Hyd. Oxalate	White cryst. solid —acid reaction.	Soluble in water.	
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Potassium Oxalate	White cryst. solid.	do.	1. 2
CH <sub>3</sub> COOK	Potassium Acetate	do. deliquescent.	do.	1. 2
KH.C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	Potassium Hyd. Tartrate	White cryst. solid —acid reaction.	Sparingly soluble in water.	1
K <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	Potassium Tartrate	White cryst. solid.	Soluble in water.	1. 2
KCN	Potassium Cyanide	Whitesolid. Odour of bitter almonds, alkaline reaction. Deep violet solid.	do.	
KMnO <sub>4</sub>	Potassium Permanganate		Soluble in water. Red- dish violet solution.	
K <sub>4</sub> Fe(CN) <sub>6</sub>	Potassium Ferrocyanide	Light yellow cryst. solid.	Soluble in water. Yel- low solution.	
K <sub>3</sub> Fe(CN) <sub>6</sub>	Potassium Ferricyanide	Reddish - orange solid.	Soluble in water. Brown solution.	
KCNS	Potassium Sulphocyanide	White cryst. solid.	Soluble in water.	
KSbO <sub>3</sub>	Potassium Metantimoniate	White solid.	Sparingly soluble in water.	
H <sub>2</sub> SiO <sub>3</sub>	Potassium Metasilicate	White glassy solid.	do.	

### Summary of Reactions for Sodium. Na.

Use a solution of Sodium Chloride ( $\text{NaCl}$ ), Nitrate ( $\text{NaNO}_3$ ), or Sulphate ( $\text{Na}_2\text{SO}_4$ ).

Reagent.	Results observed.	Remarks.
1. $\text{HCl}$	No precipitate.	
2. $\text{H}_2\text{S}$ (in presence of $\text{HCl}$ )	do.	
3. $\text{NH}_4\text{OH}$	do.	
4. $(\text{NH}_4)_2\text{S}$	do.	
5. $(\text{NH}_4)_2\text{CO}_3$	do.	
6. $\text{Na}_2\text{HPO}_4$	do.	
7. <b>Flame test</b>	On heating a small quantity of substance on Platinum wire in oxidizing flame an <b>intense yellow flame</b> is obtained if Sodium is present.	<b>Note.</b> Sodium is present in traces in most compounds; traces are also present in the air, on bench, &c., so that a feeble Sodium flame is readily given by nearly all substances. The reaction indicating the presence of Sodium is nevertheless quite definite if properly carried out. The solid should always be used. If a solution is given, evaporate carefully to dryness before taking a trace upon Platinum wire.
[8. $\text{KSbO}_3$ Potassium Metantimoniate	White precipitate of Sodium Metantimoniate, $\text{Na SbO}_3$ . $\text{KSbO}_3\text{Aq} + \text{NaClAq} = \text{NaSbO}_3 + \text{KClAq}$ This test is hardly satisfactory and is best omitted by a beginner.]	



**Summary regarding Sodium and its notable Compounds,**  
most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
Na	Metallic Sodium, m. pt. 96° C.	Brilliant yellowish lustre, but tarnishes by oxidation on exposure to air. Kept under petroleum oil.	Reacts vigorously with water, setting free Hydrogen.	Electrolysis, &c.
NaCl	Sodium Chloride	White cryst. solid.	Soluble in water.	1. 2
NaBr	Sodium Bromide	do.	do.	
NaI	Sodium Iodide	White cryst. (deliquescent).	do.	
NaNO <sub>3</sub>	Sodium Nitrate	do.	do.	1. 2
NaNO <sub>2</sub>	Sodium Nitrite	Nearly white solid —generally faint yellow tint.	do.	NaNO <sub>3</sub> and Pb.
NaHSO <sub>4</sub>	Sodium Hydrogen Sulphate	White cryst. solid —strongly acid reaction.	do.	1. 2
	Sodium Bisulphate			
Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O	Sodium Sulphate (Glauber's salt)	White cryst. solid.	do.	1. 2
Na <sub>2</sub> SO <sub>3</sub>	Sodium Sulphite	do.	do.	1
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O	Sodium Thiosulphate (often erroneously termed 'Hyposulphite')	do.	do.	Na <sub>2</sub> SO <sub>3</sub> and S.
NaHCO <sub>3</sub>	Sodium Hydrogen Carbonate Sodium Bicarbonate 'Baking Soda'	White powder.	Sparingly soluble in water. The Ammonia-Soda process depends upon this fact.	1. Ammonia-Soda process.

## Summary regarding Sodium and its notable Compounds

(continued),

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation.
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	Sodium Carbonate Soda Crystals Washing Soda	White cryst. efflorescent solid. Anhydrous $\text{Na}_2\text{CO}_3$ is a white powder.	Soluble in water.	1. Leblanc and Ammonia-Soda.
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	Sodium Phosphate	White cryst. solid.	do.	1. 2
$(\text{Na}_2\text{O})$	Sodium Oxide	Nearly white solid.	Reacts with water to give Caustic Soda.	$\text{NaNO}_3$ or $\text{Na}_2\text{O}_2$ & $\text{Na}$
$\text{Na}_2\text{O}_2$	Sodium Peroxide	Light yellow powder.	Reacts with water to give Caustic Soda and Oxygen.	Direct union.
$\text{NaOH}$	Sodium Hydroxide Caustic Soda	White solid—sticks, powder, or lumps.	Soluble in water—strongly alkaline reaction, soapy feel.	
$\text{Na}_2\text{S}$	Sodium Sulphide	White cryst. solid.	Soluble in water.	1
$\text{Na}_2\text{S}_x$	Sodium Polysulphide	Yellow solid.	Soluble in water—yellow to reddish solution.	
$\text{NaHC}_2\text{O}_4$	Sodium Hyd. Oxalate	White cryst. solid—acid reaction.	Soluble in water.	1. 2
$\text{Na}_2\text{C}_2\text{O}_4$	Sodium Oxalate	White cryst. solid.	do.	1. 2
$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$	Sodium Acetate	do.	do.	1. 2
$\text{NaH} \cdot \text{C}_4\text{H}_4\text{O}_6$	Sodium Hyd. Tartrate	do.	do.	1. 2
	Sodium Bitartrate			
$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$	Sodium Tartrate	do.	do.	1. 2
$\text{NaCN}$	Sodium Cyanide	White solid.	do.	
$\text{NaSbO}_3$	Sodium Metantimoniate	do.	Nearly insoluble in water, and its formation can be used as a test for Na, but unless in experienced hands is apt to give erroneous results.	
$\text{Na}_2\text{SiO}_3$	Sodium Silicate (Waterglass)	Glassy solid.	Slightly soluble in water.	Heat $\text{SiO}_2$ and $\text{Na}_2\text{CO}_3$ .

NOTE.—The wet tests for soluble metallic Hydroxides (i. e. tests for the free hydroxyl ion in solutions of metallic salts) are best considered after the tests for the acids (p. 215).

ANALYTICAL TABLES BASED UPON THE FOREGOING  
LISTS OF TESTS.

A study of the first and second reactions given for each metal in the preceding summaries will indicate clearly the reasons which have caused the metals to be separated into the six analytical groups summarized on p. 89. Put as concisely as possible the results are as follows:—

Metal in solution as part of a salt.	Reagent.	
	Hydrochloric Acid.	Sulphuretted Hydrogen in presence of HCl.
Silver	White pp. of Silver Chloride (AgCl).	Black pp. of Silver Sulphide (Ag <sub>2</sub> S).
Mercurous, Hg.	White pp. of Mercurous Chloride (HgCl).	Black pp. of Mercuric Sulphide (HgS) and Mercury.
Lead	White pp. of Lead Chloride (PbCl <sub>2</sub> ).	Black pp. of Lead Sulphide (PbS).
Copper	No precipitate.	Black pp. of Copper Sulphide (CuS).
Mercuric, Hg.	No precipitate.	Black pp. of Mercuric Sulphide (HgS).
Bismuth	A white pp. of BiOCl may form, but dissolves on adding more HCl and warming.	Deep brown pp. of Bismuth Sulphide (Bi <sub>2</sub> S <sub>3</sub> ).
Arsenious, As...	No precipitate.	Yellow pp. of Arsenious Sulphide (As <sub>2</sub> S <sub>3</sub> ).
Arsenic, As....	do.	No pp. with Arsenic Compounds until reduced to Arsenious condition.
Antimony	A white pp. of SbOCl may form, but dissolves on adding more HCl and warming.	Orange pp. of Antimonious Sulphide (Sb <sub>2</sub> S <sub>3</sub> ).
Stannous, Sn...	No precipitate.	Brown pp. of Stannous Sulphide (SnS).
Stannic, Sn....	do.	Yellow pp. of Stannic Sulphide (SnS <sub>2</sub> ).
Aluminium	do.	No precipitate.
Ferrous, Fe...	do.	do.
Ferric, Fe...	do.	do.
(Chromic)	do.	do.
Zinc	do.	do.
(Manganese)	do.	do.
Barium	do.	do.
(Strontium)	do.	do.
Calcium	do.	do.
Magnesium	do.	do.
Ammonium	do.	do.
Potassium	do.	do.
Sodium	do.	do.

A consideration of these results indicates that if we add **Hydrochloric Acid** (HCl) to an unknown solution of a simple salt and obtain a white precipitate which does not dissolve on adding a few more drops of acid and gently warming, **Silver** (Ag), **Mercury in the mercurous condition** (i. e.  $\text{Hg}^{\text{ous}}$  or  $\text{Hg}^{\cdot}$ ), or **Lead** (Pb) must be present. On the contrary, if we obtain no precipitate then these three metals must be absent. One must reiterate that the reason for the precipitation depends upon the insolubility of the chlorides of **Silver, Mercurous, and Lead in water**. The chlorides of all the other metals (with the exception of cuprous chloride (p. 67), which would hardly be met with in elementary analysis) are soluble in water, and are therefore not precipitated.

If we obtain no precipitate with hydrochloric acid and proceed to add **Sulphuretted Hydrogen** ( $\text{H}_2\text{S}$ ) to the same solution we might get a precipitate of **Copper Sulphide** ( $\text{CuS}$ ), **Mercuric Sulphide** ( $\text{HgS}$ ), **Bismuth Sulphide** ( $\text{Bi}_2\text{S}_3$ ), **Arsenious Sulphide** ( $\text{As}_2\text{S}_3$ ), **Antimonious Sulphide** ( $\text{Sb}_2\text{S}_3$ ), **Stannous Sulphide** ( $\text{SnS}$ ), or **Stannic Sulphide** ( $\text{SnS}_2$ ). On the other hand, if no precipitate forms, the metals Cu,  $\text{Hg}^{\text{ic}}$ , Bi, As, Sb, and Sn are proved absent. If no precipitate were obtained by these two simple tests, we would have proved the absence of nine of the metals. By further gradual elimination we can test for the metals of Groups III to VI. The tests must be carried out in an absolutely definite order, and the reason for this is well exemplified by the summary of results for hydrochloric acid and sulphuretted hydrogen (in presence of hydrochloric acid) tabulated above. If we add sulphuretted hydrogen before adding hydrochloric acid we may get the metals of Group I—Ag,  $\text{Hg}^{\text{ous}}$ , Pb—precipitated as black sulphides. This would cause difficulty in testing, as the sulphides of bismuth (Bi), copper (Cu), mercuric ( $\text{Hg}^{\cdot}$ ), and stannous ( $\text{Sn}^{\cdot}$ ) are also nearly black.

The order of adding the group reagents, the division into groups, and the reasons for the precipitation of the metals in the respective groups are indicated in the following summary:—

# THE ARRANGEMENT OF THE METALS INTO GROUPS.

Group.	Group Reagent.	Metals in group.	Substances precipitated.	Reasons for precipitation under given conditions: precautions.
I	Hydrochloric Acid ( $\text{HClAq}$ )	Ag, $\text{Hg}^{\text{ous}}$ , Pb	AgCl HgCl PbCl <sub>2</sub>	The Chlorides of Silver, Mercurous ( $\text{Hg}^{\text{ous}}$ ), and Lead are insoluble in water.
II	Sulphuretted Hydrogen ( $\text{H}_2\text{S}$ ) (in presence of $\text{HClAq}$ )	(a) Cu, $\text{Hg}^{\text{ic}}$ , Bi (b) As, Sb, $\text{Sn}^{\text{ous}}$ , $\text{Sn}^{\text{ic}}$	(a) CuS, HgS, Bi <sub>2</sub> S <sub>3</sub> (b) As <sub>2</sub> S <sub>3</sub> , Sb <sub>2</sub> S <sub>3</sub> , SnS, SnS <sub>2</sub>	The Sulphides of Cu, $\text{Hg}^{\text{ic}}$ , Bi, As, Sb, $\text{Sn}^{\text{ous}}$ , $\text{Sn}^{\text{ic}}$ are insoluble in dilute Hydrochloric Acid. Note.—HCl must be present for two reasons:— (1) If the solution be neutral or alkaline other sulphides, e.g. ZnS, might be precipitated. (2) If the solution is not acidified, As <sub>2</sub> S <sub>3</sub> and Sb <sub>2</sub> S <sub>3</sub> may not come down, as they are soluble in alkalis (pp. 109, 110).
III	Ammonium Hydroxide ( $\text{NH}_4\text{OH}$ ) in presence of Ammonium Chloride ( $\text{NH}_4\text{Cl}$ )	Al, $\text{Fe}^{\text{ous}}$ , $\text{Fe}^{\text{ic}}$ , (Cr)	Al(OH) <sub>3</sub> Fe(OH) <sub>2</sub> Fe(OH) <sub>3</sub> Cr(OH) <sub>3</sub>	The Hydroxides of Al, $\text{Fe}^{\text{ous}}$ , $\text{Fe}^{\text{ic}}$ , and Cr are insoluble in water and Ammonium Chloride solution. Note.— $\text{NH}_4\text{ClAq}$ must be added in sufficient quantity, otherwise Hydroxides of Zn, Mn, and Mg might be precipitated. (See Lists of Tests for these metals.)
IV	Ammonium Sulphide ( $(\text{NH}_4)_2\text{S}$ ) in presence of $\text{NH}_4\text{ClAq}$ and $\text{NH}_4\text{OHAq}$	Zn, (Mn)	ZnS, (MnS)	The Sulphides of Zn and Mn are insoluble in water and in $\text{NH}_4\text{ClAq}$ and $\text{NH}_4\text{OHAq}$ . Notes.—(1) $\text{NH}_4\text{ClAq}$ must be present, otherwise Mg may be precipitated. (2) The solution must be made alkaline in reaction by addition of $\text{NH}_4\text{OHAq}$ , because if $(\text{NH}_4)_2\text{S}$ be added to an acid solution, $\text{H}_2\text{S}$ is evolved and Sulphur precipitated.
V	Ammonium Carbonate ( $(\text{NH}_4)_2\text{CO}_3$ ) in presence of $\text{NH}_4\text{ClAq}$ and $\text{NH}_4\text{OHAq}$	Ba, (Sr), Ca	$\text{BaCO}_3$ , ( $\text{SrCO}_3$ ), $\text{CaCO}_3$	The Carbonates of Ba, (Sr), and Ca are insoluble in water, $\text{NH}_4\text{ClAq}$ , and $\text{NH}_4\text{OHAq}$ . Notes.—(1) $\text{NH}_4\text{ClAq}$ must be present, otherwise Mg may be precipitated. (2) $(\text{NH}_4)_2\text{CO}_3$ would be decomposed in an acid solution, therefore the solution is made alkaline with $\text{NH}_4\text{OHAq}$ .
VI	No group reagent. (a) $\text{Na}_2\text{HPO}_4\text{Aq}$ in presence of $\text{NH}_4\text{ClAq}$ and $\text{NH}_4\text{OHAq}$ (b) Boil with $\text{NaOHAq}$ (c) Flame test.	Mg   NH <sub>4</sub>  K Na	Mg. NH <sub>4</sub> . PO <sub>4</sub>   NH <sub>3</sub> is evolved.  Violet flame. Brilliant yellow flame.	Magnesium Ammonium Phosphate is insoluble in water, $\text{NH}_4\text{Cl}$ , and $\text{NH}_4\text{OHAq}$ .  All Ammonium Compounds are decomposed on boiling with Sodium Hydroxide, giving off NH <sub>3</sub> .

## 142 TESTS FOR ELECTRO-POSITIVE RADICLES

The reader should now understand why the metals are divided into analytical groups, and should be ready to proceed to the analysis of simple salts and mixtures of compounds with a fair chance of understanding the reactions which he has to carry out.

We will consider the following cases which might be met with in order, as they form a series of gradually increasing difficulty.

### A. ANALYSIS OF ANY GIVEN AQUEOUS SOLUTION OF A SIMPLE SUBSTANCE FOR A SINGLE METALLIC RADICLE.

### B. ANALYSIS OF A SIMPLE SUBSTANCE GIVEN IN THE SOLID STATE WHICH IS—

(1) SOLUBLE IN WATER.

(2) INSOLUBLE IN WATER. (a) The substance is not a phosphate or is a phosphate of a metal of Groups I or II. (b) The substance is a phosphate of a metal of Groups III, IV, V, or of Mg.

#### General Notes.

(a) Insoluble phosphates may seriously complicate analysis, and when a body is insoluble in water and a precipitate is obtained in Group III phosphoric acid must be tested for. If present it must be removed before proceeding, as indicated on p. 159.

(b) Insoluble oxalates and tartrates of metals of Groups III, IV, V, or of magnesium may complicate analysis in a similar way to the corresponding phosphates. They must be decomposed by ignition (i.e. by heating the dry substance) before proceeding with Group III.

### C. ANALYSIS OF A GIVEN AQUEOUS SOLUTION CONTAINING TWO OR MORE METALS BELONGING TO DIFFERENT ANALYTICAL GROUPS.

(NOTE.—Groups II*a* and II*b* are generally regarded as different groups, e. g. copper and arsenic might be present).

### D. ANALYSIS OF A SOLID MIXTURE CONTAINING TWO OR MORE METALS BELONGING TO DIFFERENT ANALYTICAL GROUPS, and not more than one acid radicle.

(a) Phosphates absent.

(b) Phosphates present.

**E. BRIEF SUMMARY OF ANALYSIS OF A MIXTURE, GIVEN IN SOLUTION OR IN SOLID STATE, CONTAINING TWO OR MORE METALS WHICH MAY BELONG TO THE SAME GROUP.**

(NOTE.—This hardly belongs to an elementary course and can be omitted by most candidates for elementary examinations if time does not allow.)

(a) Phosphates insoluble in water absent.

(b) Phosphates insoluble in water present.

**F. INSOLUBLE SUBSTANCES**, i. e. bodies insoluble in water and the common solvents. The treatment of these will be better understood after considering the acids. See p. 172.

---

**A. ANALYSIS OF ANY GIVEN AQUEOUS SOLUTION OF A SIMPLE SUBSTANCE FOR A SINGLE METALLIC RADICLE.**

Carry out the following preliminary tests:—

(1) Test the solution with litmus paper.

If neutral this might indicate—

(a) Pure water.

(b) A salt of neutral reaction.

If acid one might suspect—

(a) A free acid, e. g.  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{CH}_3 \cdot \text{COOH}$ .

(b) An acid salt, e. g.  $\text{NaHSO}_4$ ,  $\text{KH} \cdot \text{C}_4\text{H}_4\text{O}_6$ .

(c) A normal salt of acid reaction, e. g.  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ .

If alkaline the substance might be—

(a) A free base, e. g.  $\text{KOH}$ ,  $\text{NaOH}$ ,  $\text{Ca}(\text{OH})_2$ .

(b) A normal salt of alkaline reaction, e. g.  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{KCN}$ .

(c) A basic salt, e. g. basic lead acetate.

NOTE.—Very few basic salts are soluble in water.

(2) If the solution is acid add a pinch of solid sodium carbonate, and if effervescence takes place suspect a free acid. Evaporate 20–30 c.c. of solution to dryness, finishing the evaporation either with a very small flame, or preferably on a water bath, so as to avoid loss and decomposition of any solid residue. A beaker containing boiling water will serve for a water-bath, the basin containing the substance being placed over the beaker. If the beaker has no lip, put two small pieces of folded paper between basin and beaker to allow for escape of steam. While the evaporation is proceeding, test through the general analytical scheme and group tests detailed below (pp. 146 and 147). Any residue obtained can be used for dry tests for both bases and acids.

(3) Test a few c.c. of the original solution with sodium carbonate solution. — If no precipitate forms, one need only look for sodium, potassium, or ammonium.

(NOTE.—If the solution is acid, and causes effervescence on addition of the carbonate, continue adding carbonate solution until after effervescence ceases, and the reaction mixture is alkaline.)



## ANALYTICAL TABLES FOR DETECTION OF METALS.

**Method of procedure in using the tables:—**

(1) Carry out the tests given in order until a positive result is obtained.

(2) Try to identify the metal (or metals)—

(a) By its group reaction (column 3, p. 146);

(b) By application of confirmatory tests summarized in Tables I to VI, but more completely given under the summaries for the respective metals.

(3) Having found the metal, the student may write equations for the positive reactions he has carried out, letting X stand for the radicle of a monobasic acid,  $X_2$  for the radicle of a dibasic acid, &c. ; e. g. if copper were detected, the precipitate as sulphide might be represented by the equation



The valency table and remarks given on p. 6 should be consulted if necessary. When a student can carry out analyses for both bases and acids, it is better as a rule to wait until the acid has been detected before writing the equations expressing the positive reactions carried out.

# 146 TESTS FOR ELECTRO-POSITIVE RADICLES

Scheme of General Group Tests to be carried out in order.

Tests to be carried out in regular order.	Result observed.	Inference as to composition of precipitate.	Distinctions between substances which might be precipitated.
<p>1. To about 2 c.c. of original solution in a test-tube add dilute <b>Hydrochloric Acid</b> (<math>\text{HClAq}</math>). If a precipitate is obtained add a little more acid and warm gently. (Note.—Do not heat to boiling-point, as <math>\text{PbCl}_2</math> might go into solution.)</p>	<p>(a) White precipitate.</p> <p>(b) No precipitate.</p>	<p>(a) The substance precipitated may be <math>\text{AgCl}</math>, <math>\text{HgCl}</math>, or <math>\text{PbCl}_2</math>. (<math>\text{BiOCl}</math> and <math>\text{SbOCl}</math> might be precipitated on first adding acid, but would redissolve on adding more acid and warming.)</p> <p>(b) <math>\text{Ag}</math>, <math>\text{Hg}^{\text{ous}}</math>, and <math>\text{Pb}</math> are absent.</p>	See Table I (p. 148).
<p>2. If no precipitate, to the same portion of original solution (i.e. the portion to which <math>\text{HCl}</math> has been added) add <b>Sulphuretted Hydrogen</b> (<math>\text{H}_2\text{S}</math>), either as gas or in solution. (Note.—If gas be used be sure that the delivery tube is clean.)</p>	<p>(a) Black or brownish precipitate.</p> <p>(b) Yellow precipitate.</p> <p>(c) Orange precipitate.</p> <p>(d) No precipitate.</p>	<p>(a) Substance precipitated might be (<math>\text{PbS}</math>): <math>\text{CuS}</math>: <math>\text{HgS}</math> (characteristic changes of colour generally occur during precipitation): <math>\text{Bi}_2\text{S}_3</math>.</p> <p>(b) <math>\text{As}_2\text{S}_3</math>: <math>\text{SnS}_2</math>.</p> <p>(c) <math>\text{Sb}_2\text{S}_3</math>.</p> <p>(d) Absence of (<math>\text{Pb}</math>), <math>\text{Cu}</math>, <math>\text{Hg}^{\text{lc}}</math>, <math>\text{Bi}</math>, <math>\text{As}</math>, <math>\text{Sb}</math>, <math>\text{Sn}^{\text{ous}}</math>, <math>\text{Sn}^{\text{c}}</math>.</p>	See Tables II A and II B.
<p>3. If no precipitate, to fresh portion (about 2 c.c.) of original solution add <b>Ammonium Chloride</b> and <b>Ammonium Hydroxide</b>. (Note.—Add at least twice the volume of Ammonium Chloride to that of solution taken.)</p>	<p>(a) White gelatinous precipitate.</p> <p>(b) Greenish precipitate turning brown on the top of the solution where in contact with air.</p> <p>(c) Flocculent brown precipitate.</p> <p>(d) Greyish green precipitate.</p> <p>(e) No precipitate.</p>	<p>(a) The substance precipitated may be <math>\text{Al}(\text{OH})_3</math>. (Note.—From very strong solutions of Zinc and Magnesium Salts, white precipitates of the Hydroxides, <math>\text{Zn}(\text{OH})_2</math> and <math>\text{Mg}(\text{OH})_2</math>, might be obtained. They would dissolve on adding more Ammonium Chloride and warming.)</p> <p>(b) <math>\text{Fe}(\text{OH})_2</math>, indicating a Ferrous Compound.</p> <p>(c) <math>\text{Fe}(\text{OH})_3</math>, indicating a Ferric Compound.</p> <p>(d) <math>\text{Cr}(\text{OH})_3</math>.</p> <p>(e) Absence of <math>\text{Al}</math>, <math>\text{Fe}^{\text{ous}}</math>, <math>\text{Fe}^{\text{lc}}</math>, <math>\text{Cr}</math>.</p>	See Table III.

Scheme of General Group Tests to be carried out in order (*continued*).

Tests to be carried out in regular order.	Result observed.	Inference as to composition of precipitate.	Distinctions between substances which might be precipitated.
4. If no precipitate, to same solution (i.e. solution to which $\text{NH}_4\text{ClAq}$ and $\text{NH}_4\text{OHAq}$ have been added) add <b>Ammonium Sulphide</b> , $(\text{NH}_4)_2\text{S}$ .	(a) White precipitate. (b) Salmon - pink precipitate. (c) No precipitate.	(a) The substance precipitated may be Zinc Sulphide, $\text{ZnS}$ . (b) The precipitate may be Manganous Sulphide, $\text{MnS}$ . (c) Zinc and Manganese are absent.	See Table IV (p. 154).
5. If no precipitate, to fresh portion of original solution add $\text{NH}_4\text{ClAq}$ , $\text{NH}_4\text{OHAq}$ , and $(\text{NH}_4)_2\text{CO}_3\text{Aq}$ and warm gently.	(a) White precipitate. (b) No precipitate.	(a) The substance precipitated may be Barium Carbonate, $\text{BaCO}_3$ , Strontium Carbonate, $\text{SrCO}_3$ , or Calcium Carbonate, $\text{CaCO}_3$ . (b) Ba, Sr, and Ca are absent.	See Table V (p. 155).
6. If no precipitate, to original solution add $\text{NH}_4\text{ClAq}$ , $\text{NH}_4\text{OHAq}$ , and $\text{Na}_2\text{HPO}_4\text{Aq}$ . (Note.—One could add $\text{Na}_2\text{HPO}_4$ to solution used in Test (5) instead.)	(a) White precipitate. Formation hastened by stirring. (b) No precipitate.	(a) The substance precipitated may be Magnesium Ammonium Phosphate, $\text{MgNH}_4\text{PO}_4$ . (b) Magnesium is absent.	See Table VI.
7. If no precipitate, <b>boil</b> a few c.c. of original solution with $\text{NaOHAq}$ .	(a) Evolution of Ammonia gas, recognized by its odour and effect on moist red litmus paper. (b) No Ammonia evolved.	(a) Ammonium $(\text{NH}_4)$ Salt is present. (b) Ammonium Salt is absent.	See Table VI.
8. Evaporate a few c.c. of original solution cautiously to dryness in porcelain basin. Moisten the residue by concentrated $\text{HNO}_3$ (or $\text{HCl}$ ), take a small quantity on tip of <b>Platinum wire</b> and heat in <b>Bunsen flame</b> .	(a) Flame test is violet. (b) Flame is coloured an intense yellow.	(a) Potassium is present. (b) Sodium is present.	See Table VI.

TABLE I.

## Distinction between Silver, Mercurous, and Lead.

The white precipitate may be silver chloride ( $\text{AgCl}$ ), mercurous chloride ( $\text{HgCl}$ ), or lead chloride ( $\text{PbCl}_2$ ).

To determine which metal is present proceed as follows:—Allow the precipitate to settle, pour off the supernatant liquid, and then warm gently a small quantity of the precipitate with ammonia solution. If the precipitate is silver chloride it will dissolve, while mercurous chloride will be turned black, and lead chloride will remain white. It follows therefore that

if the precipitate dissolves, silver is indicated;

if it turns black, mercury is present;

and if it remains white, lead is the metallic radicle in the original solution.

To make certain, carry out at least a couple of confirmatory tests. Each test is carried out with about 2 c.c. of original solution.

## Confirmatory Tests.

Reagent.	Silver.	Reagent.	Mercurous.	Reagent.	Lead.
(1) $\text{K}_2\text{CrO}_4$	Deep red precipitate of Silver Chromate, $\text{Ag}_2\text{CrO}_4$ .	(1) KOH or NaOH	Black precipitate of Mercurous Oxide, $\text{Hg}_2\text{O}$	(1) $\text{K}_2\text{CrO}_4$	Yellow precipitate of Lead Chromate, $\text{PbCrO}_4$ .
(2) KOH or NaOH	Grey precipitate of Silver Hydroxide, $\text{AgOH}$ .	(2) KI	Finch-green precipitate of Mercurous Iodide, $\text{HgI}$ .	(2) KI	Yellow precipitate of Lead Iodide, $\text{PbI}_2$ , which can be recrystallized in golden spangles from boiling water (p. 60).
(3) KI	Faintly yellow precipitate of Silver Iodide, $\text{AgI}$ .	(3) $\text{K}_2\text{CrO}_4$	Reddish precipitate of Mercurous Chromate, $\text{Hg}_2\text{CrO}_4$ .	(3) $\text{H}_2\text{SO}_4\text{Aq}$	White precipitate of Lead Sulphate, $\text{PbSO}_4$ .
	For complete explanations and equations see p. 94.		See p. 96.		See p. 98.

### DISTINCTION BETWEEN THE METALS OF GROUPS II<sub>A</sub> AND II<sub>B</sub>.

The precipitate might be  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{HgS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}$ , or  $\text{SnS}_2$ .

Proceed as follows:—

Decant off the supernatant liquid and some of the precipitate (say about three-fourths) into another test-tube, and warm the remaining precipitate with yellow ammonium sulphide  $(\text{NH}_4)_2\text{S}_x$ .

If the precipitate dissolves, proceed to Table II<sub>B</sub>.

If the precipitate does not dissolve,  $\text{As}$ ,  $\text{Sb}$ ,  $\text{Sn}^{\text{ous}}$ , and  $\text{Sn}^{\text{ic}}$  are absent. ( $\text{Pb}$ ),  $\text{Cu}$ ,  $\text{Hg}^{\text{ic}}$ , or  $\text{Bi}$  might be present. To distinguish between the four latter elements two methods can be used.

#### Group II<sub>A</sub>.

**Method I.**—If the original solution were blue or green, copper is indicated, and if during precipitation a change of colour from white through yellow, brown, and black took place, mercuric mercury is probably present, and one might at once proceed to carry out the confirmatory tests for copper or mercury. Lead should have been indicated in Group I, unless the solution was extremely dilute. The addition of a few drops of potassium chromate, which would give a characteristic yellow precipitate of lead chromate if lead were present, could be used for confirmation. This would leave bismuth, which can be confirmed by the bismuth oxychloride test in the following manner: Add  $\text{NH}_4\text{OH}$  to a few c.c. of original solution. If bismuth be present a white precipitate of bismuth hydroxide,  $\text{Bi}(\text{OH})_3$ , would be obtained. Filter off this white precipitate, wash it into the apex of the filter paper, and then dissolve it in as small a quantity of hydrochloric acid as possible—say 6 to 10 drops—catching the filtrate in a test-tube. Fill up the test-tube with distilled water, when a milky precipitate of bismuth oxychloride ( $\text{BiOCl}$ ) is at once formed if bismuth is present.

Equation:  $\text{BiCl}_3\text{Aq} + \text{H}_2\text{O} = \text{BiOCl} + 2\text{HClAq}$ .

**Method II.**—Filter off the black precipitate, wash it with water on the filter, boil 2 c.c. of nitric acid (one volume of concentrated acid to two volumes of water) in a test-tube, and pour the boiling acid on the precipitate, using another test-tube to

catch what comes through. Repeat, if necessary, with the same quantity of acid (which should always be freshly boiled before pouring on to the precipitate).  $\text{PbS}$ ,  $\text{CuS}$ , and  $\text{Bi}_2\text{S}_3$  would dissolve to give solutions of nitrates. Mercuric sulphide ( $\text{HgS}$ ) would remain insoluble. [NOTE.—If the precipitate were not properly washed before adding the boiling dilute acid, even  $\text{HgS}$  might dissolve, because there might be sufficient  $\text{HCl}$  adhering to it to form aqua regia.] To the nitrate solution add excess of ammonium hydroxide,  $\text{NH}_4\text{OH}$ . Copper will give a blue coloration; bismuth and lead would give white precipitates of  $\text{Bi}(\text{OH})_3$  and  $\text{Pb}(\text{OH})_2$  respectively. If lead be suspected, test for it by the chromate and sulphuric acid tests. Test for bismuth by filtering off the white precipitate of hydroxide, dissolving it in a few drops of  $\text{HClAq}$ , and adding water to form the precipitate of oxychloride as detailed in Method I. Confirm mercury by means of  $\text{KIAq}$  and  $\text{NaOHAq}$ .

TABLE II A. (Summary from above.)

**Method I.**

- (a) If solution is green or blue, test for **copper**.
- (b) If during precipitation with  $\text{SH}_2$  change of colour took place, test for **mercury**.
- (c) If there is any reason to suspect **lead**, test for it by  $\text{K}_2\text{CrO}_4$ ; and finally,
- (d) Test for **bismuth** by the oxychloride reaction.

**Method II.**

- (a) Filter the black precipitate, wash it, and then try to dissolve in boiling dilute nitric acid. If insoluble, test for mercury by  $\text{KIAq}$ .
- (b) If soluble, add to the solution in nitric acid  $\text{NH}_4\text{OHAq}$  until reaction is alkaline. A blue coloration may indicate copper; a white precipitate, lead or bismuth.
- (c) Test the original solution for bismuth by oxychloride test, and before or after doing so test for lead by  $\text{K}_2\text{CrO}_4\text{Aq}$  and  $\text{H}_2\text{SO}_4\text{Aq}$ .

**Summary of Confirmatory Tests.**

(Carried out on original solution.)

(Pb).	Cu.	Hg <sup>lc</sup>	Bi.
(1) $\text{K}_2\text{CrO}_4$ .	(1) Flame test. Platinum wire.	(1) <i>Copper test</i> , i.e. acidify original solution with $\text{HCl}$ and boil with $\text{Cu}$ . Silvery deposit.	(1) <b>Oxychloride test</b> .
(2) $\text{H}_2\text{SO}_4\text{Aq}$ .	(2) $\text{K}_1\text{Fe}(\text{CN})_6$ .	(2) $\text{NaOH}$ .	(2) $\text{KI}$ .
(3) $\text{KI}$ .	(3) $\text{NH}_4\text{OHAq}$ .	(3) $\text{KI}$ .	(3) $\text{K}_2\text{CrO}_4$ — Do not confuse the pp. obtained with Lead Chromate.
(4) Reduction on Charcoal.			
For complete explanation and equations, see p. 98.	See p. 100.	See p. 102.	See p. 104.

TABLE II B.

Distinction between As, Sb,  $\text{Sn}^{\text{ous}}$ , and  $\text{Sn}^{\text{ic}}$ .

If the precipitate given by  $\text{SH}_2$  in presence of  $\text{HCl}$  dissolves in yellow ammonium sulphide,  $(\text{NH}_4)_2\text{S}_x$ , then As, Sb,  $\text{Sn}^{\text{ous}}$ , or  $\text{Sn}^{\text{ic}}$  may be present.

If the precipitate is brown, stannous tin is indicated; if orange, antimony; and if yellow, arsenic or stannic tin. Stannous tin is therefore readily distinguished by colour, and, after a little practice, the orange colour of antimonious sulphide is recognized. To distinguish between the two yellow precipitates, As and  $\text{Sn}^{\text{ic}}$ , warm a small quantity of the precipitate with  $(\text{NH}_4)_2\text{CO}_3\text{Aq.}$   $\text{As}_2\text{S}_3$  dissolves,  $\text{SnS}_2$  (and  $\text{Sb}_2\text{S}_3$ ) do not. Use the following confirmatory tests:—

As.	Sb.	Stannous Tin.	Stannic Tin.
(1) Reinsch's test.	(1) $\text{NH}_4\text{OHAq.}$	(1) $\text{HgCl}_2\text{Aq.}$ Grey pp. of Mercury.	(1) Reduce to Stannous by nascent Hydrogen Zn and $\text{HClAq}$ —then add $\text{HgCl}_2\text{Aq}$ [Note.—The Zinc should preferably be pure.]
(2) Dry test $\text{Na}_2\text{CO}_3$ and powdered substance in hard glass tube.	(2) Precipitation of Oxychloride ( $\text{SbOCl}$ ), soluble in Tartaric Acid.	(2) $\text{KOHAq.}$	
(3) Fumes on charcoal—garlic odour.	(3) Reinsch.		
For complete explanations and equations, see p. 106.	(4) Dry test.		
	See p. 110.	See p. 112.	See p. 112.



TABLE III.

Distinction between Al, Fe<sup>ous</sup>, Fe<sup>ic</sup>, Cr.

The colours of the different precipitates are sufficient guides in this group, and one could at once proceed to the confirmatory tests.

The greyish green precipitate of chromium hydroxide, Cr(OH)<sub>3</sub>, is readily distinguished from the greenish precipitate of ferric hydroxide, because the latter becomes brown on the top on shaking with air, owing to oxidation to ferric hydroxide, Fe(OH)<sub>3</sub>.

NOTE.—From concentrated solutions of Zn, Mn, or Mg compounds, white precipitates may be obtained in this group, because of the difficulty of adding a sufficiency of ammonium chloride (NH<sub>4</sub>Cl) to prevent precipitation of the hydroxides of the metals. These white precipitates are flocculent, and not gelatinous like the precipitate of aluminium hydroxide, Al(OH)<sub>3</sub>. On decanting off the supernatant liquids, and warming the residue with ammonium chloride, solution will be effected. Aluminium hydroxide is insoluble in ammonium chloride.

Carry out the following confirmatory tests:—

Al.	Fe <sup>ous</sup> .	Fe <sup>ic</sup> .	Cr.
<p>(1) <b>KOH</b> or <b>NaOH</b>. White precipitate soluble in excess.</p> <p>(2) Moisten filter paper first with a concentrated solution of substance and then with <b>Co(NO<sub>3</sub>)<sub>2</sub></b> and ignite.—<b>Blue residue.</b></p> <p>For complete explanations and equations, see p. 114.</p>	<p>(1) <b>K<sub>3</sub>Fe(CN)<sub>6</sub></b>. Dark blue precipitate.—Turnbull's blue.</p> <p>(2) <b>K<sub>4</sub>Fe(CN)<sub>6</sub></b>. Gives a light blue precipitate of potassium ferrous ferrocyanide, K<sub>2</sub>Fe·[Fe(CN)<sub>6</sub>]</p> <p>See p. 116.</p>	<p>(1) <b>K<sub>3</sub>Fe(CN)<sub>6</sub></b>. No precipitate.</p> <p>(2) <b>K<sub>4</sub>Fe(CN)<sub>6</sub></b>. Gives a deep blue precipitate of Prussian blue.</p> <p>See p. 116.</p>	<p>(1) <b>KOH</b> or <b>NaOH</b>. Greyish green precipitate of Chromium Hydroxide.</p> <p>(2) Fuse up in a hard glass tube or iron spoon with <b>KNO<sub>3</sub></b> or <b>Na<sub>2</sub>O<sub>2</sub></b>—mass turns yellow—extract with water, acidify with <b>Acetic Acid</b> and add <b>Lead Acetate</b>,—yellow pp. of <b>Lead Chromate</b> is formed.</p> <p>See p. 118.</p>

TABLE IV.

## Distinction between Zn and Mn.

The colour of the precipitate at once indicates which metal should be confirmed. The precipitate of zinc sulphide may look yellow because of the yellow colour of the ammonium sulphide  $(\text{NH}_4)_2\text{S}$ , but if filtered off and washed its real colour will be apparent.

## Confirmatory Tests:

<p style="text-align: center;"><b>Zn.</b> Indicated by <b>white precipitate</b> of <b>ZnS</b>.</p>	<p style="text-align: center;"><b>Mn.</b> Indicated by <b>salmon-pink</b> precipitate of <b>MnS</b>.</p>
<p>(1) <b>KOH</b> or <b>NaOH</b>. White precipitate of Zinc Hydroxide, <math>\text{Zn}(\text{OH})_2</math>, soluble in excess to give a solution of Aluminate.</p> <p>(2) Moisten a few square centimetres of filter paper first with a concentrated solution of the substance and then with <math>\text{Co}(\text{NO}_3)_2</math> and ignite. Yellowish green mass is obtained.</p> <p>For complete explanations and equations, see p. 120.</p>	<p>(1) <b>KOH</b> or <b>NaOH</b>. White precipitate of Manganous Hydroxide, <math>\text{Mn}(\text{OH})_2</math>, which rapidly turns brown.</p> <p>(2) Heat on charcoal with <math>\text{Na}_2\text{CO}_3</math> and <math>\text{KNO}_3</math> or <math>\text{Na}_2\text{O}_2</math>. A green mass is obtained which gives a green solution of Sodium Manganate. On dilution the solution turns pink.</p> <p>See p. 122.</p>

TABLE V.

## Distinction between Ba, Sr, and Ca.

Two cases might be met with: (1) Sr presumably absent.

(2) Sr perhaps present.

## 1. Sr presumably absent.

Ca and Ba are readily distinguished by adding  $\text{CaSO}_4\text{Aq}$  to the original solution. If a precipitate forms, Ba is present; if not, Ca. Confirm as below.

## 2. Sr may be present.

(a) Filter off the white precipitate of carbonate, and wash the precipitate into the apex of the filter paper. Test by platinum wire moistened with HCl.

Ba gives a light green flame.

Sr gives a pink flame.

Ca gives a brick-red flame.

(b) Dissolve the precipitate in a few drops of acetic acid, and add to half of the solution obtained  $\text{K}_2\text{CrO}_4\text{Aq}$ .—Yellow precipitate of barium chromate insoluble in acetic acid indicates Ba.

(c) If there is no precipitate, in order to distinguish between Sr and Ca add to the other half of the solution  $\text{CaSO}_4\text{Aq}$ . Warm gently and allow to stand five minutes. White precipitate indicates strontium.

## Confirmatory Tests:

	Ba	Sr.	Ca.
(1) Platinum wire test	Green flame	Crimson flame	Brick-red flame
(2) $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$	White pp.	White pp.	White pp.

TABLE VI.

The tests already given are sufficiently distinctive, but the following tests applied to the original solution might be used for confirmation :—

Mg.	NH <sub>4</sub> .	K.	Na.
<p>(1) <b>NaOH</b> aq. White precipitate soluble in Ammonium Chloride.</p> <p>(2) <b>A pink residue</b> is obtained after moistening filter paper first with a concentrated solution of the substance and then with <b>Co(NO<sub>3</sub>)<sub>2</sub></b> and igniting.</p> <p>For list of tests with equations, see p. 130.</p>	<p>No further test is necessary. The odour and alkaline reaction of Ammonia are characteristic.</p> <p>See p. 132.</p>	<p>Confirm by evaporating a portion of original solution to dryness, dissolving in a few drops of water, placing in a test-tube, and adding an equal quantity of Tartaric Acid or Sodium Hydrogen Tartrate solution. Shake the tube violently, closing the top with the thumb; if no precipitate forms, scratch the side of the tube inside the liquid by rubbing with a glass rod.</p> <p>(Note.—The addition of a few drops of alcohol may aid precipitation, but should be employed with caution.)</p> <p>See p. 134.</p>	<p>No further test beyond that of the flame is advisable. This should if possible be invariably carried out with the solid substance as already indicated.</p> <p>See p. 136.</p>

## B. ANALYSIS OF A SIMPLE SUBSTANCE GIVEN IN THE SOLID STATE.

**Preliminary Note regarding solution.** In the case of a substance given in the solid state, the method of procedure followed would vary with the analyst's knowledge of chemistry. It is not always advisable to carry out dry tests if time be limited, but it should be noted that the appearance of the body taken in conjunction with a few dry tests may often give a clue as to the most suitable solvent; e.g. if the substance were a heavy orange powder insoluble in water, which gave a malleable bead which marked paper by heating on charcoal, the substance would presumably be lead oxide, and the best solvent in the circumstances would be dilute nitric acid. A decision of this sort, however, means considerable acquaintance with the subject, and it is advisable that the beginner should have a definite scheme to fall back upon. A convenient method is as follows:—

(1) Take in a test tube as much solid as would occupy the volume of a small drop of water (say about 0.05 c.c.) and boil with 4–5 c.c. of distilled water. If the substance dissolves, proceed with the general analytical scheme detailed above (A, p. 144).

(2) If the substance does not seem to dissolve, pour off the water, and add about 4–5 c.c. of dilute HCl (or add about 1 c.c. of concentrated HCl to the water), warm carefully, and finally boil. If the substance dissolves, note whether any effervescence takes place, indicating carbonate, &c., as detailed under Acids (p. 186), and then proceed with tests as in A, omitting the addition of HCl to test for Group I.

(3) If the substance does not dissolve in dilute HCl, pour off the dilute acid and add about 2 c.c. of concentrated acid and boil. If solution is effected, add more solid gradually and continue boiling until solid remains undissolved. Then dilute with water and filter.

**NOTES.**—(a) If chlorine is evolved, a peroxide or oxidizing agent is indicated, e.g.  $\text{PbO}_2 + 4\text{HCl} = \text{PbCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$ .

(b) If a heavy white crystalline precipitate separates on dilution with water or on cooling, lead is probably present, as precipitate will probably be  $\text{PbCl}_2$ .

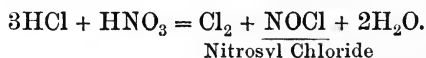
(4) If the substance does not dissolve in conc. HCl, wash out the test-tube, put in a fresh quantity of the solid, and boil with

dilute nitric acid. If solution is effected, proceed as with concentrated HCl, i. e. add more solid, and boil until no more solid is taken up. Dilute with water, and carry out the general tests detailed under A (p. 144).

(5) If substance does not dissolve, try concentrated nitric acid. Proceed as with concentrated HCl and dilute  $\text{HNO}_3$ .

(NOTE.—Many nitrates, e.g.  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ , are nearly insoluble in concentrated nitric acid, but easily soluble in water. They may separate during boiling with the strong acid, but will dissolve on diluting with water.)

(6) **Aqua regia**, a mixture of hydrochloric and nitric acids, might be next tried. A minimum quantity of the mixture and a minimum quantity of nitric acid in the mixture should be employed. Proceed as follows: Add about 1 c.c. of concentrated HCl to the solid, and then add three or four drops of concentrated  $\text{HNO}_3$ , boil, and if solution seems to be effected, add if necessary a few more drops of nitric acid. **Aqua regia owes its powerful solvent properties chiefly to the presence of nascent chlorine produced by the following decomposition:—**

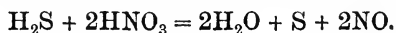


(7) In a few cases, e.g. if substance be yellow and  $\text{As}_2\text{S}_3$  is suspected, it is much better to dissolve in concentrated hydrochloric acid with addition of a crystal of potassium chlorate, rather than in nitric acid. Using HCl and  $\text{KClO}_3$  a solution is obtained which reacts readily with  $\text{H}_2\text{S}$ , whereas dissolving in  $\text{HNO}_3$  no reaction will take place with  $\text{H}_2\text{S}$  until the arsenic in solution is reduced to the arsenious state.

#### General Notes regarding solution :

(1) If anything stronger than dil. HCl has been used, and if the solution is strongly acid, evaporate nearly to dryness in the fume cupboard before going on to test for metals.

(2) In getting a substance into solution a student should aim at using the least possible quantity of acid. Excess of acid, especially  $\text{HNO}_3$ , tends to prevent sulphides coming down in Group II, e.g.  $\text{H}_2\text{S}$  is at once destroyed by  $\text{HNO}_3$ .



It is no uncommon thing to find a beginner effecting solution with about 10 c.c. of aqua regia. Such a solution is almost

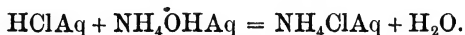
valueless for analytical work. It must be evaporated nearly to dryness in the fume cupboard to get rid of excess of acid, and then diluted with water before proceeding.

Having effected solution, it is sufficient as a rule to proceed through the Scheme of General Tests as detailed under A, p. 144.

Under certain conditions, however, e.g. (a) when insoluble Phosphates are present, and (b) when insoluble Oxalates or Tartrates are present, a modification of the General Scheme must be employed as follows:—

(a) Insoluble Phosphates present.

If phosphates insoluble in water are present they may cause trouble during analysis. Phosphates insoluble in water, i.e. phosphates of metals other than Na, K, or  $\text{NH}_4$ , are all soluble in  $\text{HClAq}$  and in  $\text{HNO}_3\text{Aq}$ . On adding  $\text{NH}_4\text{OHAq}$  to their solutions, however, they are precipitated, as the ammonium hydroxide neutralizes the acid which keeps them in solution; e.g.  $\text{Zn}_3(\text{PO}_4)_2$ ,  $\text{Ca}_3(\text{PO}_4)_2$ , and  $\text{Mg}_3(\text{PO}_4)_2$  are insoluble in water, but easily soluble in  $\text{HClAq}$ , indicating absence of metals of Group I. If one tests the solution systematically for metals, no reaction is obtained with  $\text{H}_2\text{S}$ , indicating absence of metals of Group II, but on adding  $\text{NH}_4\text{ClAq}$  and  $\text{NH}_4\text{OHAq}$  to test for Group III, the original substances are precipitated because the  $\text{NH}_4\text{OHAq}$  neutralizes the acid used for dissolving them.



As the above phosphates are white they might easily be mistaken for  $\text{Al}(\text{OH})_3$ . In such a case it is impossible to get the group tests for Zn, Ca, and Mg until the phosphoric acid has been removed. This is generally effected by adding  $\text{FeCl}_3\text{Aq}$  under suitable conditions, and eliminating the acid from solution as ferric phosphate,  $\text{FePO}_4$ .

Method of Procedure:—

Boil the filtrate from Group II until all the  $\text{SH}_2$  has been removed and then test about 1 c.c. of solution for iron with  $\text{K}_4\text{Fe}(\text{CN})_6$  or  $\text{K}_3\text{Fe}(\text{CN})_6$ . If ferrous iron be in solution (and if it has been necessary to add  $\text{H}_2\text{S}$  in presence of iron it will be present), boil the solution with 1–2 c.c. of conc.  $\text{HNO}_3\text{Aq}$  for ten minutes to oxidize any ferrous to ferric. Neutralize the solution by cautious addition of  $\text{NH}_4\text{OH}$  to the solution placed

## 160 TESTS FOR ELECTRO-POSITIVE RADICLES

in a porcelain basin, with constant stirring until the reaction is nearly neutral to litmus.

A precipitate may form. Add 10–15 c.c. of ammonium acetate (prepared by adding acetic acid to  $\text{NH}_4\text{OHAq}$  until the reaction is just acid). Then add  $\text{FeCl}_3\text{Aq}$  drop by drop until the supernatant liquid has a reddish tint. Boil, filter, and wash. The ferric chloride added precipitates all the phosphoric acid, because ferric phosphate is insoluble in acetic acid. The filtrate is tinted reddish.

On boiling the solution after excess of iron has been added, the excess of iron, and aluminium if present, are precipitated as basic acetate. Chromium too may be precipitated as hydroxide, so that after boiling until the liquid is seen to be colourless, all the iron, and probably all the Al and Cr, are removed from the solution.

Test (A) the Filtrate and (B) the Residue separately.

A. Filtrate. Proceed to test through the groups as usual. Test for Groups III, IV, V, and VI. Fe and probably Al will be absent. Cr may be present.

B. Residue. The residue should be tested for Al and Cr by one of the following two methods:—

### Method I.

Put the washed residue in a dish with a little water, add about a gram of solid sodium peroxide, boil and filter. The residue will be  $\text{Fe}(\text{OH})_3$ . The solution may contain Al as sodium aluminate,  $\text{Al}(\text{ONa})_3$ , and chromium as chromate.

- (a) Test for Al by acidifying one half with  $\text{HClAq}$  and then adding excess of  $\text{NH}_4\text{OH}$  and boiling. White gelatinous pp. of  $\text{Al}(\text{OH})_3$  indicates aluminium.
- (b) Test the other half for chromium by acidifying with acetic acid and adding lead acetate. A yellow pp. of  $\text{PbCrO}_4$  indicates chromium.

### Method II.

If  $\text{Na}_2\text{O}_2$  is not available, proceed as follows:—

- (a) Boil up the residue with caustic soda. Filter. Acidify with  $\text{HCl}$  and then add  $\text{NH}_4\text{OHAq}$  and boil. White pp. of  $\text{Al}(\text{OH})_3$  indicates aluminium.
- (b) Fuse up the residue with  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  on platinum foil or in a small iron spoon. Extract with water and



filter. The solution will be yellowish if chromium be present. Acidify with acetic acid and add lead acetate. Yellow precipitate of  $\text{PbCrO}_4$  indicates chromium.

---

(b) **Oxalates or Tartrates insoluble in water present.** If oxalate or tartrate insoluble in water be indicated on heating a small quantity of dry substance, heat strongly about a gram of the substance until the organic compounds are completely decomposed; dissolve the residue in dil.  $\text{HCl}$  or dil.  $\text{HNO}_3$ ; filter if necessary and proceed as usual through the groups.

### C. ANALYSIS OF A SOLUTION CONTAINING TWO OR MORE METALS BELONGING TO DIFFERENT ANALYTICAL GROUPS.

**Preliminary Note.**—In testing a solution containing two or more metals, the general scheme of analysis detailed under A (p. 144) is followed, but a few precautions are necessary to avoid mistakes.

(1) One must test for all metals (except the Ammonium group) with the same portion of the solution.

(2) A metal of an earlier group must be completely eliminated from the solution before a metal of a later group is tested for.

To indicate how important this statement is, suppose we consider what might happen if one started to test a concentrated solution of lead nitrate for more than one metal, and did not take care to eliminate the lead in Groups I and II. One could obtain the following results:—

Test for Group I. Add a few drops of  $\text{HClAq.}$ —A white pp. of  $\text{PbCl}_2$  forms.

Test for Group II. Filter, and to filtrate add  $\text{H}_2\text{S}$  in small quantity.—A black pp. of  $\text{PbS}$  comes down.

Test for Group III. Filter, boil off the  $\text{H}_2\text{S}$ , and to same solution add  $\text{NH}_4\text{ClAq}$  and a few drops of  $\text{NH}_4\text{OHAq.}$ —A white pp. of  $\text{Pb(OH)}_2$  is obtained.

Test for Group IV. Filter, and to same solution add  $(\text{NH}_4)_2\text{S}$  in small quantity.—A black pp. of  $\text{PbS}$  appears.

Test for Group V. Filter, and to same solution add a small quantity of  $(\text{NH}_4)_2\text{CO}_3\text{Aq.}$ —A white pp. of  $\text{PbCO}_3$  is thrown down.

Test for Mg in Group VI. Filter, and to same solution add a few drops of  $\text{Na}_2\text{HPO}_4\text{Aq.}$ —A white pp. of  $\text{Pb}_3(\text{PO}_4)_2$  forms.

Lead might thus be made to appear in all the groups, and as many other metals, e.g. Ag,  $\text{Hg}^{\text{ous}}$ ,  $\text{Hg}^{\text{ic}}$ , Bi, Cu, would behave similarly, the student will appreciate how important it is to get rid of one metal before going on to test for the next.

(3) Always carry out preliminary tests before going on to any particular group, and if no metal of that group be present, do not add the reagent for its precipitation to the bulk

of the solution, but pass on, discarding the small quantity of solution used in the preliminary test.

The exact method of procedure would be as follows:—

(1) To solution add a few drops of HCl, until solution is distinctly acid. If a precipitate comes down, continue adding HClAq as long as a pp. forms, filter, and as soon as a few drops have run through, test the filtrate by addition of another couple of drops of HCl. If no pp. forms, one can go on to test the filtrate for Group II. If, however, a precipitate does form, one must mix the different portions of the liquid, add more HCl until precipitation is complete, and then pass the liquid through a fresh filter paper.

NOTE.—If in carrying out this test one warms the solution to aid precipitation, the reaction mixture should be thoroughly cooled before filtration by holding under the tap, to ensure precipitation of as much lead chloride as possible should it chance to be present.

(2) Preliminary Test. About 1 c.c. of the filtrate can be tested for Group II by adding excess of  $\text{SH}_2$ , and one should keep in view the fact that if lead be present as indicated by the precipitation of the characteristic heavy crystalline precipitate (soluble in boiling water) with HClAq, a slight black precipitate of PbS is certain to come down in Group II, since  $\text{PbCl}_2$  is slightly soluble in water, while PbS is almost insoluble. Lead is the only metal which can come down in two groups if the scheme of testing indicated is correctly carried out. If lead is present, and the black precipitate in Group II is small in amount, one can filter it off and reserve it for further examination after testing through the remaining groups. If a precipitate is obtained in the preliminary test, add excess of  $\text{H}_2\text{S}$  to the bulk of the solution, warm and filter. Test the first few drops of filtrate by addition of  $\text{H}_2\text{S}$  so as to make sure of complete precipitation.

NOTE.—If the preliminary test indicates that no metal of Group II is present, it is better to proceed at once to Group III, without adding  $\text{H}_2\text{S}$ , because  $\text{H}_2\text{S}$  reduces ferric salts to ferrous, as indicated below.

(3) Expel the  $\text{SH}_2$  from the filtrate by boiling for a few minutes, and then add  $\text{NH}_4\text{ClAq}$  and  $\text{NH}_4\text{OHAq}$  to about 2 c.c. If a greenish pp. forms which seems to be ferrous hydroxide,  $\text{Fe}(\text{OH})_2$ , test another small quantity with  $\text{K}_3\text{Fe}(\text{CN})_6$ . If a deep blue

pp. (Turnbull's blue) comes down, indicating that a ferrous compound is present, it is necessary to oxidize the ferrous salt to ferric before proceeding further if one intends to test for metals in succeeding groups. To do this, add about 1 c.c. of concentrated  $\text{HNO}_3$  to the solution, and boil for a few minutes. Then add  $\text{NH}_4\text{Cl}$  and excess of  $\text{NH}_4\text{OH}$ , when the iron will be precipitated completely as  $\text{Fe}(\text{OH})_3$ . This conversion of ferrous iron to ferric is necessary, because ferrous iron is not completely precipitated by  $\text{NH}_4\text{OH}$ , and trouble would be caused in the next group by a trace of iron passing through into the filtrate. Make certain that precipitation is complete, as in previous groups.

NOTE.—The presence of a ferrous salt as indicated by above tests does not indicate that the iron was present in the ferrous state. All ferric salts are reduced to ferrous by  $\text{SH}_2$ , e.g.



If iron be present, the original solution must be tested with  $\text{K}_3\text{Fe}(\text{CN})_6$ .

(4) To a few drops of the filtrate from Group III add  $(\text{NH}_4)_2\text{SAq}$ . If a pp. forms, add excess of  $(\text{NH}_4)_2\text{SAq}$  and filter.

(5) Filter and test a small quantity with  $(\text{NH}_4)_2\text{CO}_3$ , and warm gently. If a pp. forms, warm the solution and then add excess of  $(\text{NH}_4)_2\text{CO}_3\text{Aq}$ ; filter.

(6) To a few c.c. of the filtrate add  $\text{Na}_2\text{HPO}_4\text{Aq}$ , and warm. If a pp. forms, divide the residual liquid into two parts.

(a) Add slight excess of  $\text{Na}_2\text{HPO}_4\text{Aq}$  to one half, filter and evaporate to dryness. Ignite, to get rid of ammonium salts, and reserve the residue for carrying out confirmatory tests for potassium if detected.

(b) Evaporate the other half of the solution to dryness, ignite, to get rid of ammonium salts, and then moisten with a few drops of  $\text{HNO}_3$  and test for potassium and sodium by platinum wire. Use blue glass or potassioscope if necessary.

(7) Boil the original solution with excess of  $\text{NaOHAq}$  to test for ammonium salts.

**Precautionary Note.**—It is obvious that one cannot test the filtrate from Group V for ammonium compounds, because  $\text{NH}_4\text{ClAq}$ ,  $\text{NH}_4\text{OHAq}$ , or  $(\text{NH}_4)_2\text{CO}_3\text{Aq}$  may have been added previously, and one would therefore be certain to obtain a positive result. This is a fundamental mistake of the beginner in analysis.

He uses reagents, and then tests the solution for a metallic or acid radicle which he has added. Another common mistake, for example, is to dissolve a substance in  $\text{HClAq}$ , and then test for a chloride. See remarks under Acids.

**Confirmatory Tests.** Although after detection of a metal by the group tests one can frequently use the original solution for confirmatory tests, even when two or more metals are present, this is not invariably the case. Suppose, for example, that one thought one had identified lead in a solution which really contained a barium salt and not a lead salt. One might select as two confirmatory tests the precipitation of chromate on addition of  $\text{K}_2\text{CrO}_4\text{Aq}$ , and the precipitation of sulphate on adding dil.  $\text{H}_2\text{SO}_4$ . The Ba present would give a yellow pp. of  $\text{BaCrO}_4$  and a white pp. of  $\text{BaSO}_4$  respectively, which a beginner might mistake for  $\text{PbCrO}_4$  and  $\text{PbSO}_4$  respectively.

**Rule.** If in doubt, one can generally proceed as follows:—

Wash the precipitate obtained in carrying out the group reaction for the metal. One obtains in this way a pure compound of the metal, which can usually be dissolved in an appropriate solvent and tested by the usual confirmatory tests. It may be necessary that the solution obtained should be made nearly neutral before carrying out certain confirmatory tests; e.g.  $\text{K}_2\text{CrO}_4\text{Aq}$  added to a strongly acid solution of a silver salt gives no pp. of silver chromate, because that body is soluble in acids.

The conditions for precipitation in the different cases are fully indicated under the Lists of Tests for the respective metals. To neutralize a solution, place it in a porcelain dish, add a drop of litmus, and then add  $\text{NH}_4\text{OHAq}$  or dil.  $\text{HNO}_3\text{Aq}$  with constant stirring until the reaction is approximately neutral. The following summary indicates concisely the method of procedure:—

# 166 TESTS FOR ELECTRO-POSITIVE RADICLES

Test.	Result.	Confirmatory Tests.
Note:—Filtration is unnecessary unless a pp. forms.		
1. Add to solution <b>HClAq</b> as long as a pp. forms. Filter.	Pp. may be <b>AgCl</b> <b>HgCl</b> <b>PbCl<sub>2</sub></b>	(Add <b>NH<sub>4</sub>OHAq</b> to pp.; <b>AgCl</b> dissolves; <b>HgCl</b> blackens; <b>PbCl<sub>2</sub></b> does not dissolve. Confirm further with original solution. Usetests on p. 148.
2. To filtrate add excess of <b>SH<sub>2</sub></b> . Filter.	Pp. may be <b>(PbS)</b> <b>CuS</b>  <b>HgS</b> <b>Bi<sub>2</sub>S<sub>3</sub></b> <b>As<sub>2</sub>S<sub>3</sub></b> <b>Sb<sub>2</sub>S<sub>3</sub></b> <b>SnS</b> <b>SnS<sub>2</sub></b>	(1) <b>K<sub>2</sub>CrO<sub>4</sub></b> . (2) <b>H<sub>2</sub>SO<sub>4</sub></b> . (1) <b>NH<sub>4</sub>OH</b> . (2) Flame test. (3) <b>K<sub>4</sub>Fe(CN)<sub>6</sub></b> . (1) <b>Cu</b> and <b>HCl</b> . (2) <b>SnCl<sub>2</sub></b> . (1) Oxychloride test. (2) <b>KI</b> . (1) Reinsch's test. (1) <b>NH<sub>4</sub>OH</b> . (2) Reinsch. <b>HgCl<sub>2</sub></b> . <b>HgCl<sub>2</sub></b> after appropriate treatment.
3. Boil off <b>H<sub>2</sub>S</b> and then add <b>NH<sub>4</sub>ClAq</b> and <b>NH<sub>4</sub>OHAq</b> in excess. Filter. N.B. Ferrous Salts must be oxidized to ferric before adding <b>NH<sub>4</sub>ClAq</b> and <b>NH<sub>4</sub>OHAq</b> .	Pp. may be <b>Fe(OH)<sub>3</sub></b> <b>Al(OH)<sub>3</sub></b> <b>(Cr(OH)<sub>3</sub>)</b>	(Dissolve the pp. in minimum of dilute hot <b>HClAq</b> , and carry out confirmatory tests given on p. 153.
4. To filtrate add <b>(NH<sub>4</sub>)<sub>2</sub>S</b> in excess. Filter.	Pp. may be <b>ZnS</b> <b>MnS</b>	(Dissolve in minimum of dil. <b>HCl</b> , and confirm as described on p. 154.
5. To filtrate add <b>(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub></b> in excess. Filter.	Pp. may be <b>BaCO<sub>3</sub></b> <b>(SrCO<sub>3</sub>)</b> <b>CaCO<sub>3</sub></b>	(Dissolve in minimum of acetic or <b>HClAq</b> , and confirm as described on p. 155.
6. To half the filtrate add <b>Na<sub>2</sub>HPO<sub>4</sub>Aq</b> . Filter.	Pp. may be <b>Mg.NH<sub>4</sub>.PO<sub>4</sub></b> .	This pp. is of little value for carrying out confirmatory tests. If necessary, the original solution after removal of metals in first five groups and evaporation to dryness and ignition should be used.
7. Evaporate half the filtrate from (5) to dryness, and ignite to get rid of Ammonium Salts. Moisten with <b>HNO<sub>3</sub></b> and test with Platinum wire.	<b>K</b> or <b>Na</b> may be indicated.	(Confirm Potassium by precipitation of Potassium Hydrogen Tartrate by dissolving residue in a few drops of water and adding Tartaric Acid or Sodium Hydrogen Tartrate (see p. 156).
8. Test the original solution for Ammonium Compounds by boiling up with <b>NaOHAq</b> or <b>KOHAq</b> .	Evolution of <b>NH<sub>3</sub></b> .	No further test necessary.

#### D. ANALYSIS OF A SOLID MIXTURE CONTAINING TWO OR MORE METALS BELONGING TO DIFFERENT ANALYTICAL GROUPS.

(Groups II A and II B might be regarded as different groups.)

The substance must be obtained in solution before going on to the wet tests, and the remarks made under B would, generally speaking, apply in this case; e. g. one generally tries (a) water, (b) dil. HCl, (c) conc. HCl, (d) dil.  $\text{HNO}_3$ , (e) conc.  $\text{HNO}_3$ , and (f) aqua regia, in order, unless the appearance of the body or any preliminary dry tests which one may have carried out has indicated what would probably be the best solvent. Attention should be given to the following points:—

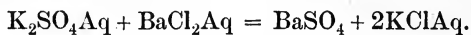
(1) If anything stronger than dilute HCl is required for solution, the student should be particularly careful to use a minimum of acid. Boil up with excess of solid for some time (e. g. 5 minutes), dilute with water, filter, and use solution for testing through the groups in the usual way. If the solution seems to be strongly acid after filtering, evaporate nearly to dryness, and add water before proceeding to Group II.

(2) A mixture often consists of one substance soluble in water, and of one substance insoluble in water, but soluble in acids. In such a case by far the best method of procedure may be to boil up with water, filter, and use the filtrate for testing for one metal, and the carefully washed residue on the filter for testing for the other. If one dissolves both substances in acid, the mixture may become more difficult to analyse. e. g. Suppose the two substances are lead oxide and magnesium sulphate. The magnesium sulphate is easily soluble in water, and might be dissolved and analysed without difficulty: the residue of litharge would from appearance and reactions be quite easy to identify. Suppose, however, that the two substances are dissolved in  $\text{HClAq}$  or  $\text{HNO}_3\text{Aq}$ . If  $\text{HClAq}$  is used a mixed precipitate of lead chloride,  $\text{PbCl}_2$ , and lead sulphate,  $\text{PbSO}_4$ , will form during the experiment, and if  $\text{HNO}_3\text{Aq}$  be used,  $\text{PbSO}_4$  will come down. The identification of  $\text{PbSO}_4$  might present difficulties to a beginner.

(3) If more than one acid be present in the mixture, the difficulties are considerably increased, because there is greater chance of two soluble bodies interacting to give insoluble products; e. g. barium chloride and potassium sulphate given in a mixed

## 168 TESTS FOR ELECTRO-POSITIVE RADICLES

solid would interact immediately on solution in water, with precipitation of barium sulphate,  $\text{BaSO}_4$ , which a beginner would probably find very difficult.



Having dissolved the substance in an appropriate solvent, carry out the analysis as follows:—

(a) If Phosphates insoluble in water are absent, proceed as described under C, p. 162.

(b) If Phosphates insoluble in water are present, the Phosphoric Acid must as a rule be eliminated by the method described under B, p. 159.



**E. SUMMARY OF ANALYSIS OF A MIXTURE, GIVEN IN SOLUTION OR IN SOLID STATE, CONTAINING TWO OR MORE METALS WHICH MAY BELONG TO THE SAME GROUP.**

In analysing a mixture which may contain two or more metals in one group, the methods of solution already given would apply, and it is important to note that separate analysis of extracts with (a) Water, and (b) Hydrochloric Acid, might give suggestive results. Any residue insoluble in water and hydrochloric acid should be examined separately, and if a portion is found to be quite insoluble in the ordinary solvents, Section F should be consulted (p. 171). Dry tests are often of great value. A larger quantity of substance should be taken for solution than in previous cases.

Having effected solution and got rid of as much acid as possible, proceed to the systematic analysis outlined in following table : —

# GENERAL TABLE. EXAMINATION FOR METALLIC RADICLES.

Experiment.	Result.	Distinction and Confirmation.
1. To the solution add $\text{HClAq}$ as long as a precipitate forms. Filter.	Precipitate may be $\text{AgCl}$ $\text{HgCl}$ $\text{PbCl}_2$ .	} Examine by General Table I.
2. Test a small quantity of filtrate with $\text{H}_2\text{SAq}$ , and if a pp. forms pass gaseous $\text{SH}_2$ into the rest of filtrate in a small flask. (Note proper method of saturating as explained on p. 146.) Filter and wash with $\text{H}_2\text{SAq}$ . Reserve filtrate for Expt. 4.	Precipitate may be:— ( $\text{PbS}$ ), $\text{HgS}$ , $\text{Bi}_2\text{S}_3$ , $\text{CuS}$ . $\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ , $\text{SnS}$ , or $\text{SnS}_2$ .	
3. Pierce the filter, wash the residue in a flask or test-tube, and digest at moderate temperature with $(\text{NH}_4)_2\text{S}$ . Filter.	(a) Residue insoluble in $(\text{NH}_4)_2\text{S}$ might be:— ( $\text{PbS}$ ), $\text{HgS}$ , $\text{Bi}_2\text{S}_3$ , $\text{CuS}$ . (b) The following sulphides might go into solution in the $(\text{NH}_4)_2\text{S}$ . $\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ , $\text{SnS}$ , $\text{SnS}_2$ .	} Examine by General Table II A. } Examine the solution by General Table II B.
4. Boil up filtrate until free from $\text{H}_2\text{S}$ , and then test a few c.c. for Group III by adding $\text{NH}_4\text{ClAq}$ and $\text{NH}_4\text{OH}$ and warming. If a positive result be obtained, test solution for Iron by $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ , and also for Phosphoric Acid by warming a few c.c. with excess of Ammonium Nitromolybdate. If ferrous Iron be present, oxidize it to ferric state by boiling up with about one c.c. of conc. $\text{HNO}_3$ , and if $\text{H}_3\text{PO}_4$ be present, remove it as described on p. 160. Then add $\text{NH}_4\text{ClAq}$ and $\text{NH}_4\text{OH}$ ; warm, filter.	Precipitate may be:— $\text{Al}(\text{OH})_3$ , $\text{Fe}(\text{OH})_3$ , $\text{Cr}(\text{OH})_3$ .	} Examine by General Table III.
5. Test a small quantity of filtrate with $(\text{NH}_4)_2\text{S}$ . If a pp. forms, add $(\text{NH}_4)_2\text{S}$ in slight excess, warm and filter.	Precipitate might be $\text{ZnS}$ or $\text{MnS}$ .	
6. To a few c.c. of filtrate add $(\text{NH}_4)_2\text{CO}_3\text{Aq}$ , and warm gently. If a precipitate forms, add $(\text{NH}_4)_2\text{CO}_3\text{Aq}$ to the bulk of the solution, warm and filter.	Precipitate may be $\text{BaCO}_3$ . ( $\text{SrCO}_3$ ) $\text{CaCO}_3$	} Examine by General Table V.
7. Test a small portion of filtrate with $\text{Na}_2\text{HPO}_4\text{Aq}$ . If a pp. forms, add this reagent to half the filtrate, warm and set aside for a few minutes.	Precipitate may be $\text{Mg} \cdot \text{NH}_4 \cdot \text{PO}_4$	
8. Examine the other half of the filtrate from Expt. 6 for Potassium and Sodium by evaporation to dryness and ignition to get rid of Ammonium Salts, and then employing flame test.—Platinum wire.	Flame test may indicate $\text{K}$ or $\text{Na}$ .	} Resummarized in General Table VI.
9. While above evaporation is proceeding, boil a few c.c. of original solution with $\text{NaOHAq}$ or $\text{KOH}$ .	Evolution of $\text{NH}_3$ indicates $(\text{NH}_4)$ compound.	

F. NOTEWORTHY SUBSTANCES, MANY OF WHICH ARE OF CHARACTERISTIC APPEARANCE, AND SOME OF WHICH ARE DIFFICULTLY SOLUBLE OR INSOLUBLE.

A few of the more insoluble substances commonly met with are worth special comment. Many have characteristic appearance and properties.

(1) **Metallic lustre.** The metals, e. g. Pb, Bi, Ag (these three are soluble in  $\text{HNO}_3$ ). Arsenic has greyish lustre (soluble in  $\text{HNO}_3$ ). Powdered zinc is generally bluish grey and dissolves in  $\text{HClAq}$  or  $\text{H}_2\text{SO}_4\text{Aq}$ , giving off hydrogen which can be burnt. Certain sulphides (mostly of natural occurrence) may have metallic lustre, e. g.  $\text{FeS}_2$  (pyrites),  $\text{Sb}_2\text{S}_3$  (stibnite),  $\text{PbS}$  (galena),  $\text{Cu}_2\text{S}$ ,  $\text{Fe}_2\text{S}_3$  (copper pyrites),  $\text{FeS}$  (ferrous sulphide, formed by direct union of Fe and S).

(2) **Black or brown.** Many sulphides and a few oxides, e. g.  $\text{FeS}$  (pp<sup>d</sup>),  $\text{Bi}_2\text{S}_3$ ,  $\text{PbS}$  (pp<sup>d</sup>),  $\text{CuS}$ ,  $\text{SnS}$ ,  $\text{HgS}$  (pp<sup>d</sup>),  $\text{Sb}_2\text{S}_3$  (black variety),  $\text{CuO}$ ,  $\text{PbO}_2$  (very dark brown),  $\text{MnO}_2$ .

(3) **Yellow.**  $\text{HgO}$  (yellow variety),  $\text{PbI}_2$ ,  $\text{As}_2\text{S}_3$ , ( $\text{As}_2\text{S}_5$ ),  $\text{SnS}_2$  (sometimes in crystals similar to  $\text{PbI}_2$ ),  $\text{PbCrO}_4$ ,  $\text{BaCrO}_4$ ,  $\text{Ag}_3\text{PO}_4$ ,  $\text{Ag}_3\text{AsO}_3$ , ( $\text{PbO}$  massicot).

Faint yellow.  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{FePO}_4$ .

(4) **Orange or Brownish.**  $\text{Sb}_2\text{S}_3$  (deep orange),  $\text{PbO}$  (light brown, litharge),  $\text{Ag}_3\text{AsO}_4$  (chocolate brown).

(5) **Red.**  $\text{HgO}$  (red variety),  $\text{HgI}_2$ ,  $\text{Pb}_3\text{O}_4$  (red lead),  $\text{HgS}$  cinnabar (red) and vermilion (scarlet).

(6) **White substances particularly insoluble.**  $\text{Sb}_2\text{O}_5$ ,  $\text{SnO}_2$ ,  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{CaSO}_4$  (is slightly soluble),  $\text{AgCl}$ ,  $\text{HgCl}$  (calomel).

Many substances are met with in a variety of forms, e. g. mercuric oxide  $\text{HgO}$  (red and yellow), mercuric sulphide  $\text{HgS}$  (black, red, and scarlet), antimony sulphide  $\text{Sb}_2\text{S}_3$  (greyish metallic lustre, black or orange). The solubility of above substances has in most cases been previously mentioned, but a few notes might be found useful:—

(1) Many oxides with more oxygen than corresponds to the ordinary valency of the metal, e. g.  $\text{PbO}_2$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{MnO}_2$ , yield chlorine on heating with conc.  $\text{HCl}$ .

(2) **Manganese Dioxide** and conc.  $\text{H}_2\text{SO}_4$  are convenient reagents for testing halides insoluble in cold water, e. g.

$\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{SbOCl}$ ,  $\text{BiOCl}$ ,  $\text{HgI}_2$ ,  $\text{HgI}$ ,  $\text{PbI}_2$ .

[NOTE.—Halogen can be detected in such substances as dimercurous ammonium chloride (black precipitate),  $\text{NH}_2 \cdot \text{Hg}_2\text{Cl}$ , and

in mercuric ammonium chloride (white precipitate),  $\text{NH}_2\text{HgCl}$ , by the same reagents.]

(3) As already noted, certain sulphides (e.g.  $\text{FeS}_2$ ,  $\text{As}_2\text{S}_3$ ,  $\text{HgS}$ ) give off  $\text{H}_2\text{S}$  only in small quantity on treatment with conc.  $\text{HCl}$  or aqua regia, the bulk of the sulphur being transformed to  $\text{H}_2\text{SO}_4$ . The sulphuric acid can be tested for as usual with  $\text{Ba}(\text{NO}_3)_2\text{Aq}$  and  $\text{HNO}_3\text{Aq}$  (or  $\text{BaCl}_2\text{Aq}$  and  $\text{HClAq}$ ), and, being found, conclusively proves the presence of sulphide, taking into consideration appearance and properties.

(4) Slightly soluble bodies, e.g.  $\text{CaSO}_4$ ,  $\text{PbCl}_2$ , should be kept in view while preparing solutions.

(5) Many substances behave in a characteristic manner with certain reagents; e.g. (a) Red lead turns brown on addition of  $\text{HNO}_3\text{Aq}$ , owing to separation of lead peroxide, while lead nitrate will be found in solution.

(b) Metallic  $\text{Sb}$  and  $\text{Sn}$  react with  $\text{HNO}_3$ , giving brown fumes of  $\text{NO}_2$  with separation of white insoluble powders,  $\text{Sb}_2\text{O}_5$  and  $\text{SnO}_2$ . If the latter substances be given for analysis they can be reduced on charcoal, the metals dissolved in conc.  $\text{HCl}$  (with crystal of chlorate in the case of antimony), and the solutions tested.

(6) Certain organic compounds in solution, e.g.

$\text{CaC}_2\text{O}_4$ ,  $\text{CaC}_4\text{H}_4\text{O}_6$ ,  $\text{K.SbO.C}_4\text{H}_4\text{O}_6$ , and  $\text{Hg}(\text{CN})_2$ ,

do not give all the tests for the respective metals until the organic material is got rid of. This is easily effected in the case of tartrate and oxalate by heating strongly, when oxide or carbonate of metal is left, and in the case of mercury cyanide by heating with  $\text{HClAq}$ .

(7) Many substances, quite insoluble in the ordinary reagents, e.g.  $\text{BaSO}_4$  and  $\text{AgCl}$ , may be obtained in soluble form by mixing the dry powdered substance with solid  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$  and heating for some time in a crucible by means of a blowpipe or special burner.

The metal is generally transformed into carbonate by such treatment—silver compounds, however, yield metal—and the acid radicle combines with sodium to give a salt soluble in water, e.g.  $\text{BaSO}_4 + \text{Na}_2\text{CO}_3 = \text{BaCO}_3 + \text{Na}_2\text{SO}_4$ .

On powdering up the residue and extracting with water, the sodium salt dissolves and the solution can be tested for the acid radicle after acidifying. The portion insoluble in water can be dissolved in  $\text{HClAq}$  or  $\text{HNO}_3\text{Aq}$  and tested for metal in the usual way, e.g.  $\text{BaCO}_3 + 2\text{HClAq} = \text{BaCl}_2\text{Aq} + \text{H}_2\text{O} + \text{CO}_2$ .

This procedure is rarely necessary in Elementary Analysis.

# IDENTIFICATION AND SEPARATION OF METALS OF GROUP I.

## GENERAL TABLE I.

The precipitate obtained on addition of **HClAq** to original solution may contain **AgCl**, **HgCl**, and **PbCl<sub>2</sub>**. After filtering, wash the precipitate on the filter paper with boiling water until free from **PbCl<sub>2</sub>** if present.

(NOTE.—When the liquid coming through gives no reaction with **SH<sub>2</sub>Aq**, the washing is sufficient.)

<p>Filtrate may contain <b>PbCl<sub>2</sub>Aq</b>. Confirm by addition of a) <b>K<sub>2</sub>CrO<sub>4</sub>Aq</b>. b) <b>KIAq</b>. Yellow pp. in each case confirms <b>Pb</b>.</p>	<p>White residue may be <b>AgCl</b>, <b>HgCl</b>. Warm Ammonia slightly in a test-tube and pour on to this white residue. <b>AgCl</b> dissolves and passes through. <b>HgCl</b> blackens.</p>	
	<table> <tr> <td data-bbox="347 854 631 1163"> <p>The solution may contain <b>AgCl</b>. Make acid with <b>HNO<sub>3</sub>Aq</b>. —If white curdy pp. of <b>AgCl</b> forms, <b>Ag</b> is present.</p> </td><td data-bbox="631 854 917 1163"> <p>The residue on the filter would be black Dimercurous Ammonium Chloride, <b>NH<sub>2</sub>.Hg<sub>2</sub>Cl</b>. Dissolve in a few drops of aqua regia, nearly neutralize, add Cu, strip and warm. Grey deposit on the copper, which becomes silvery on rubbing, confirms <b>Hg<sup>ous</sup></b>.</p> </td></tr> </table>	<p>The solution may contain <b>AgCl</b>. Make acid with <b>HNO<sub>3</sub>Aq</b>. —If white curdy pp. of <b>AgCl</b> forms, <b>Ag</b> is present.</p>
<p>The solution may contain <b>AgCl</b>. Make acid with <b>HNO<sub>3</sub>Aq</b>. —If white curdy pp. of <b>AgCl</b> forms, <b>Ag</b> is present.</p>	<p>The residue on the filter would be black Dimercurous Ammonium Chloride, <b>NH<sub>2</sub>.Hg<sub>2</sub>Cl</b>. Dissolve in a few drops of aqua regia, nearly neutralize, add Cu, strip and warm. Grey deposit on the copper, which becomes silvery on rubbing, confirms <b>Hg<sup>ous</sup></b>.</p>	

## IDENTIFICATION AND SEPARATION OF METALS OF GROUP II.

## (1) GENERAL TABLE II A.

## Identification and Separation of the Metals of Group II A.

After digesting the precipitate obtained on adding sulphuretted hydrogen with  $(\text{NH}_4)_2\text{S}$ , and filtering, the residue may contain  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{HgS}$ , and  $\text{Bi}_2\text{S}_3$ . Wash the precipitate free from  $\text{HClAq}$  if necessary. Boil up a mixture of about 1 c.c. of conc.  $\text{HNO}_3$  and 2 c.c. water in a test-tube, and pour on to the precipitate. Collect the filtrate in a test-tube and repeat. The residue may be  $\text{HgS}$ , or, if white,  $\text{PbSO}_4$ . The solution might contain nitrates of  $\text{Pb}$ ,  $\text{Cu}$ , and  $\text{Bi}$ .

Treatment of Solution.		Treatment of Residue ( $\text{HgS}$ ).
<p>Test a small quantity of solution with <math>\text{H}_2\text{SO}_4\text{Aq}</math>. If a pp. is obtained, add a sufficiency of <math>\text{H}_2\text{SO}_4\text{Aq}</math> and equal bulk of alcohol to main portion of solution. Filter. The precipitate may be <math>\text{PbSO}_4</math>. Filtrate may contain Copper and Bismuth Nitrates.</p>		<p>Dissolve in a few drops of aqua regia, boil off the Chlorine, nearly neutralize with <math>\text{NaOHAq}</math>, but still keep distinctly acid, add a strip of Copper and boil. The Copper strip becomes grey, and if dried and then rubbed between filter paper, silvery. This confirms <math>\text{Hg}^{\text{ic}}</math>.</p>
<p><b>Confirmation of Lead.</b></p> <p>Dissolve <math>\text{PbSO}_4</math> in Ammonium Acetate by boiling. Cool and add <math>\text{K}_2\text{CrO}_4</math>. Yellow pp. of <math>\text{PbCrO}_4</math> forms, confirming <b>Pb</b>.</p> <p><b>Note.</b>—Ammonium Acetate solution for this test can be made by adding Acetic Acid to about 2 c. c. of conc. <math>\text{NH}_4\text{OHAq}</math> until the reaction is acid.</p>	<p><b>Examination of solution which may contain Bismuth and Copper Nitrates.</b></p> <p>Add <math>\text{NH}_4\text{OHAq}</math> in excess. If solution turns blue, <b>Copper</b> is indicated. A white precipitate is probably <math>\text{Bi}(\text{OH})_3</math>. Filter.</p>	
	<p><b>Confirm Bi.</b></p> <p>Dissolve the pp. in a few drops of dil. <math>\text{HCl}</math>. Fill up the test-tube used as receiver with water. A white pp. of <math>\text{BiOCl}</math> confirms <b>Bi</b>.</p>	<p><b>Confirm Cu.</b></p> <p>Add Acetic Acid until solution is acid, and then add <math>\text{K}_4\text{Fe}(\text{CN})_6</math>. Brown coloration or precipitate of <math>\text{Cu}_2\text{Fe}(\text{CN})_6</math> confirms <b>Cu</b>.</p>

## (2) GENERAL TABLE II (B).

## Identification and Separation of the Metals of Group II B.

The solution of ammonium polysulphide may contain arsenic, antimony, and tin as thiosalts. Add  $\text{HClAq}$  to the solution until the reaction is acid.  $\text{As}_2\text{S}_5$ ,  $\text{Sb}_2\text{S}_5$ , and  $\text{SnS}_2$  are precipitated, and also sulphur, from the excess of ammonium polysulphide. Filter and wash. Pierce the filter paper, wash the residue into a small flask, add about 10 c.c. ammonium carbonate solution and one or two small pieces of solid ammonium carbonate. Digest for five to ten minutes at moderate temperature. Arsenic sulphide will dissolve, antimony and tin sulphides are almost insoluble. Filter and wash.

Treatment of filtrate.	Treatment of Residue.	
Acidify with $\text{HClAq}$ when $\text{As}_2\text{S}_3$ may be precipitated. Filter, wash; dissolve the pp. in a few drops of conc. $\text{HCl}$ with a crystal of Potassium Chlorate. Boil down until all Chlorine has been got rid of, dilute and divide into two parts: a) Add $\text{H}_2\text{SAq}$ or pass $\text{SH}_2$ . Yellow pp. of $\text{As}_2\text{S}_3$ forms. b) Add a strip of Copper, boil, and carry out the Reinsch test.	Dissolve the residue in conc. $\text{HCl}$ (with addition of a crystal of $\text{KClO}_3$ if necessary). Evaporate down, dilute with water, and place in a dish with a small piece of pure stick Zinc rolled in a piece of Platinum foil. Antimony, if present, will deposit on the Platinum as a black stain, and Tin on the Zinc.	
	Confirmation of Antimony.  Wash the Platinum with water, and put in a shallow dish with a few c.c. of water and a few drops of $(\text{NH}_4)_2\text{S}$ . Evaporate to dryness on a water-bath. The stain on the Platinum is coloured orange, owing to formation of $\text{Sb}_2\text{S}_3$ , which confirms Sb.	Confirmation of Tin.  Scrape off any deposit from the Zinc, and boil it up with conc. $\text{HCl}$ (preferably in presence of a piece of Platinum). Stannous Chloride is obtained. Dilute and add one or two drops of Mercuric Chloride ( $\text{HgCl}_2\text{Aq}$ ). A white precipitate changing to a grey deposit of Mercury confirms Tin.

## GENERAL TABLE III.

The precipitate may consist of  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{Cr}(\text{OH})_3$ . Dissolve in  $\text{HClAq}$ , and then boil for some time with  $\text{NaOHAq}$ . (NOTE.--The caustic alkali used should be free from alumina. If uncertain regarding this point a check experiment is necessary.)

The aluminium hydroxide dissolves to form sodium aluminate,  $\text{Al}(\text{ONa})_3$ . The iron and chromium hydroxides remain unaltered. Filter.

Treatment of Filtrate.	Treatment of Residue.	
Acidify the solution of Sodium Aluminate with $\text{HCl}$ , and then add $\text{NH}_4\text{OH}$ and warm. If $\text{Al}$ be present, a white gelatinous pp. of $\text{Al}(\text{OH})_3$ will come down. <b>Aluminium.</b>	Dissolve by warming with $\text{HCl}$ , and divide into two parts.	
	<p style="text-align: center;"><b>Part I.</b></p> <p>Test for Iron by <math>\text{K}_4\text{Fe}(\text{CN})_6</math>. Deep blue pp. (Prussian blue) indicates <b>Iron.</b></p>	<p style="text-align: center;"><b>Part II.</b></p> <p>Nearly neutralize with <math>\text{NaOHAq}</math>, add <b>fresh bleaching powder</b> solution, and warm. Solution turns yellow. Acidify with Acetic Acid and add <b>Lead Acetate</b>. Yellow pp. of <math>\text{PbCrO}_4</math> indicates <b>Chromium.</b></p>



## GENERAL TABLE IV.

The precipitate formed on adding ammonium sulphide may consist of **ZnS** and **MnS**. Wash the precipitate off the filter and dissolve in **HClAq.** Add **NaOHAq** in excess and boil. The manganese precipitates as manganous hydroxide, while the zinc is first precipitated as zinc hydroxide, which dissolves in excess to form sodium zincate, **Zn(ONa)<sub>2</sub>Aq.**

Treatment of Filtrate.	Treatment of Residue.
<p>To the filtrate add <b>(NH<sub>4</sub>)<sub>2</sub>SAq.</b>  White pp. of Zinc Sulphide indicates  <b>Zinc.</b>  Confirm by dissolving the Zinc Sulphide in a few drops of <b>HCl</b>, pouring on to filter paper, moistening with Cobalt Nitrate, and igniting.  <b>Green mass</b> confirms  <b>Zinc.</b></p>	<p>Dissolve the residue in <b>HCl</b> and add <b>(NH<sub>4</sub>)<sub>2</sub>SAq.</b>  Salmon pink pp. of <b>MnS</b> indicates  <b>Manganese.</b>  Confirm by dissolving in <b>HClAq</b>, avoiding excess, and then warming with bleaching powder solution.  Brownish black pp. of <b>MnO<sub>2</sub>. xH<sub>2</sub>O</b> confirms  <b>Manganese.</b></p>

GENERAL TABLE V.

The precipitate obtained with  $(\text{NH}_4)_2\text{CO}_3$  may consist of  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ . Boil acetic acid in a test-tube and pour on to the filter, and repeat if necessary, using what has come through the filter paper. A solution containing acetates is obtained. Add  $\text{K}_2\text{CrO}_4\text{Aq}$  in slight excess, and filter if a pp. forms.

Precipitate.	Filtrate.		
<p>Yellow precipitate indicates  <b>Barium.</b>            Confirm by flame test.  <b>Barium.</b></p>	<p>To half the filtrate, which may contain solutions of Strontium and Calcium Acetates, add <math>\text{CaSO}_4\text{Aq}</math>, warm gently, and allow to stand ten minutes. White precipitate may be <b>Strontium Sulphate, <math>\text{SrSO}_4</math>.</b></p>		
	<table> <tr> <td> <p>Filter pp. of <math>\text{SrSO}_4</math> and confirm Strontium by Platinum wire test.  <b>Strontium.</b></p> </td><td> <p>If a pp. was obtained with <math>\text{CaSO}_4\text{Aq}</math>, add to the other half of the filtrate a concentrated solution of Ammonium Sulphate, boil and then cool, and allow to stand ten minutes. The Strontium should be entirely precipitated as Strontium Sulphate, while the Calcium will partly remain in solution as Calcium Sulphate. Filter, and add <math>(\text{NH}_4)_2\text{C}_2\text{O}_4</math>. A white pp. of Calcium Oxalate indicates  <b>Calcium.</b>            Filter and confirm by Platinum wire test.</p> </td></tr> </table>	<p>Filter pp. of <math>\text{SrSO}_4</math> and confirm Strontium by Platinum wire test.  <b>Strontium.</b></p>	<p>If a pp. was obtained with <math>\text{CaSO}_4\text{Aq}</math>, add to the other half of the filtrate a concentrated solution of Ammonium Sulphate, boil and then cool, and allow to stand ten minutes. The Strontium should be entirely precipitated as Strontium Sulphate, while the Calcium will partly remain in solution as Calcium Sulphate. Filter, and add <math>(\text{NH}_4)_2\text{C}_2\text{O}_4</math>. A white pp. of Calcium Oxalate indicates  <b>Calcium.</b>            Filter and confirm by Platinum wire test.</p>
<p>Filter pp. of <math>\text{SrSO}_4</math> and confirm Strontium by Platinum wire test.  <b>Strontium.</b></p>	<p>If a pp. was obtained with <math>\text{CaSO}_4\text{Aq}</math>, add to the other half of the filtrate a concentrated solution of Ammonium Sulphate, boil and then cool, and allow to stand ten minutes. The Strontium should be entirely precipitated as Strontium Sulphate, while the Calcium will partly remain in solution as Calcium Sulphate. Filter, and add <math>(\text{NH}_4)_2\text{C}_2\text{O}_4</math>. A white pp. of Calcium Oxalate indicates  <b>Calcium.</b>            Filter and confirm by Platinum wire test.</p>		

## GENERAL TABLE VI.

The solution on filtration, after adding  $(\text{NH}_4)_2\text{CO}_3$ , might contain magnesium, potassium, and sodium. Divide into two parts.

(a) Small portion.	(b) Major portion.
Add $\text{Na}_2\text{HPO}_4\text{Aq}$ to about a fourth of solution, stir, and allow to stand. If Magnesium Ammonium Phosphate, $\text{Mg} \cdot \text{NH}_4 \cdot \text{PO}_4$ , comes down, the presence of <b>Magnesium</b> is indicated.	Evaporate to dryness in a porcelain dish, and ignite until all Ammonium Compounds are volatilized. Test the residue for <b>Sodium</b> and <b>Potassium</b> by the flame test (using a blue glass or potassioscope if necessary). If <b>Potassium</b> is indicated, confirm by the Potassium Hydrogen Tartrate test.

**Note.** In testing for **Ammonium Salts** by heating with caustic soda or potash the original solution must be employed.

# MEMORANDA

## MEMORANDA

# MEMORANDA

## **PART IV**

**A. IDENTIFICATION OF ACID RADICLES**

**B. IDENTIFICATION OF METALLIC OXIDES  
AND HYDROXIDES**

## PART IV

### A. IDENTIFICATION OF ACID RADICLES

### B. IDENTIFICATION OF METALLIC OXIDES AND HYDROXIDES

#### A. IDENTIFICATION OF ACID RADICLES.

The Acids cannot be tested for so systematically as the Bases, but the student should have a general scheme to fall back upon for any particular type of analysis.

A few general points must be noted :—

(1) **Solubility.** The solubility of the different salts of the metals found should be carefully kept in view throughout the analysis ; e. g. if the substance was soluble in water, and barium has been found, it is useless to look for sulphuric acid, because barium sulphate is practically insoluble in water, and similarly, if silver has been found in a simple solution, it is useless to look for chloride.

(2) In dealing with solids, the appearance of the substance given should agree with the properties of the substances detected by analysis, and the student should find the **lists of common compounds** of the metals given on the **pages adjoining the tests for the respective metals** helpful in coming to a decision as to what substances could possibly be present.

In a preliminary course a selection of acids must be made. The following list contains those in the **Conjoint Boards' Syllabus** (with a few additions placed within brackets).



## List of Acids.

Acid.	Formula.	Name of Salts.	Remarks.
Carbonic Acid	$\text{H}_2\text{CO}_3$	Carbonates	Pure Carbonic Acid, $\text{H}_2\text{CO}_3$ , is unknown. The acid is only known in solution $\text{H}_2\text{CO}_3\text{Aq}$ .
Sulphuretted Hydrogen	$\text{H}_2\text{S}$	Sulphides	The acid is a gas of feebly acid reaction in solution.
Hydrocyanic Acid (Prussic Acid)	$\text{HCN}$	Cyanides	The acid and its soluble salts are very poisonous. Care should be exercised in working with them.
Acetic Acid	$\text{CH}_3 \cdot \text{COOH}$	Acetates	The free acid might be met with.
(Sulphurous Acid)	$(\text{H}_2\text{SO}_3)$	(Sulphites)	The pure acid is unknown. A solution $\text{H}_2\text{SO}_3\text{Aq}$ smells strongly of $\text{SO}_2$ .
(Nitrous Acid)	$(\text{HNO}_2)$	(Nitrites)	The pure free acid is unknown.
Sulphuric Acid	$\text{H}_2\text{SO}_4$	Sulphates	The free acid might be met with.
Hydrochloric Acid	$\text{HCl}$	Chlorides	do.
Hydrobromic Acid	$\text{HBr}$	Bromides	The free acid would rarely be met with.
Hydriodic Acid	$\text{HI}$	Iodides	do.
Nitric Acid	$\text{HNO}_3$	Nitrates	The free acid might be met with.
Phosphoric Acid	$\text{H}_3\text{PO}_4$	Phosphates	do.
Tartaric Acid	$\text{H}_2 \cdot \text{C}_4\text{H}_4\text{O}_6$	Tartrates	do. White cryst. solid.
Oxalic Acid	$\text{H}_2 \cdot \text{C}_2\text{O}_4$	Oxalates	do. do.
Arsenious Acid	$\text{H}_3\text{AsO}_3$	Arsenites	Arsenious Anhydride, $\text{As}_2\text{O}_3$ , which gives a very dilute solution of the acid on boiling with water, is a common substance.
Arsenic Acid	$\text{H}_3\text{AsO}_4$	Arsenates	The acid or its anhydride ( $\text{As}_2\text{O}_5$ ) might be met with.

In order that a candidate may be able to consider what acids should be following **Tables of Solubility**

Class of Salts.	Solubility in water.	Solubility in Hydrochloric Acid.
1. Carbonates	The normal and acid Carbonates of <b>Na, K, NH<sub>4</sub></b> are soluble in water. All other Carbonates are insoluble, except the <b>acid Carbonates</b> (or <b>Bicarbonates</b> ) of <b>Ca, Sr, Ba, Mg, Fe, Mn</b> , which latter substances would not be met with in elementary analysis.	All are decomposed without exception, <b>CO<sub>2</sub></b> being evolved. In the case of the Carbonates of Lead and Silver, white precipitates of the Chlorides of the metals would come down during the reaction.
2. Sulphides	The Sulphides of <b>Na, K</b> , and <b>NH<sub>4</sub></b> are soluble in water. Those of <b>Ca, Sr, Ba</b> , and <b>Mg</b> are slowly decomposed by water, forming soluble Hydrosulphides and Hydroxides. The other Sulphides are insoluble.	Most Sulphides are decomposed and dissolved, <b>SH<sub>2</sub></b> being evolved, readily recognized by its odour and reaction on paper moistened with Lead Acetate. <b>HgS, FeS<sub>2</sub>, As<sub>2</sub>S<sub>3</sub></b> are not attacked by <b>HCl</b> , and <b>PbS, Ag<sub>2</sub>S, Bi<sub>2</sub>S<sub>3</sub></b> , and <b>CuS</b> only slightly.
3. Cyanides	The Cyanides of <b>Na, K, NH<sub>4</sub>, Ca, Sr, Ba</b> , and <b>Hg</b> are soluble in water. <b>AgCN</b> is insoluble, but readily dissolves in <b>KCNAq</b> .	All Cyanides are decomposed by <b>HCl</b> with evolution of <b>HCN</b> , being converted into Chlorides.
4. Acetates	All are soluble in water. Those of <b>Ag</b> and <b>Hg<sup>ous</sup></b> are only sparingly soluble.	Soluble as a rule, but Chlorides of <b>Pb, Ag</b> , and <b>Hg<sup>ous</sup></b> would be precipitated.
[5. Sulphites	Sulphites of <b>Na, K, NH<sub>4</sub></b> and a few <b>Bisulphites</b> ( <b>Na, K, NH<sub>4</sub>, Ca, Ba, Mg</b> ) are soluble in water.	All are decomposed by <b>HCl</b> with evolution of <b>SO<sub>2</sub></b> , easily recognized by its odour of burning Sulphur.
[6. Nitrites	The Nitrites of <b>Na, K, (NH<sub>4</sub>)</b> are easily soluble in water. Many others are sparingly soluble, e. g. <b>AgNO<sub>2</sub></b> .	All are decomposed, giving fumes of Oxides of Nitrogen.
7. Sulphates	Most Sulphates are soluble in water. Those of <b>Ba, Sr</b> , and <b>Pb</b> are nearly insoluble. <b>CaSO<sub>4</sub></b> is sparingly soluble (about 0.2%).	Hydrochloric Acid aids the solution in some cases.

looked for, taking into consideration the metals which he has found, the may be found convenient :—

Solubility in Nitric Acid.	Solubility in Aqua Regia.	Remarks.
All without exception—CO <sub>2</sub> is evolved.	All without exception—CO <sub>2</sub> is evolved (see note in col. 3 on Pb and Ag).	All Carbonates insoluble in water should be dissolved in HClAq or HNO <sub>3</sub> Aq, depending upon the metal present. If Ag or Pb be the metal, HNO <sub>3</sub> would obviously be more suitable than HCl, which would decompose the Carbonate, but at the same time cause a precipitation of the metals as Chlorides.
Most Sulphides are decomposed by HNO <sub>3</sub> . Very little H <sub>2</sub> S would come off in many cases, because of interaction with the HNO <sub>3</sub> . $\text{H}_2\text{S} + 2\text{HNO}_3 = 2\text{H}_2\text{O} + \text{NO} + \text{S}$ $\text{S} + 2\text{HNO}_3 = \text{H}_2\text{SO}_4 + 2\text{NO}$ HgS is unattacked. PbS, Ag <sub>2</sub> S, Bi <sub>2</sub> S <sub>3</sub> , CuS, are dissolved in boiling Nitric Acid of moderate concentration, the Sulphur being chiefly oxidized to Sulphuric Acid, H <sub>2</sub> SO <sub>4</sub> . As <sub>2</sub> S <sub>3</sub> is oxidized to Arsenic Acid, H <sub>3</sub> AsO <sub>4</sub> .	All are decomposed—the bulk of the Sulphur in most cases being transformed into Sulphuric Acid. H <sub>2</sub> SO <sub>4</sub> . HgS is transformed into HgCl <sub>2</sub> and H <sub>2</sub> SO <sub>4</sub> . As <sub>2</sub> S <sub>3</sub> is oxidized chiefly to Arsenic Acid and H <sub>2</sub> SO <sub>4</sub> .	A few somewhat intractible Sulphides, e.g. HgS, FeS <sub>2</sub> , and As <sub>2</sub> S <sub>3</sub> , can be dissolved chiefly as Chlorides with evolution of part of the Sulphur as H <sub>2</sub> S, by boiling up the powdered substance with conc. HCl, and then adding two or three drops of HNO <sub>3</sub> Aq and warming. The best solvent for As <sub>2</sub> S <sub>3</sub> is a small quantity of conc. HCl and a crystal of KClO <sub>3</sub> , which gives a solution of AsCl <sub>3</sub> in HCl readily precipitable by H <sub>2</sub> S.
All are decomposed.	All are decomposed.	KCN is the most common Cyanide. NaCN or Hg(CN) <sub>2</sub> might be met with, but only rarely.
All are soluble.	All are soluble.	The most important Acetates are those of Na, K, NH <sub>4</sub> , and Pb.
All are decomposed with liberation of SO <sub>2</sub> . Part would be oxidized to Sulphate.	Decomposed and transformed to Chloride and Sulphate.	— ]
All are decomposed.	All are decomposed.	KNO <sub>3</sub> , NaNO <sub>3</sub> , and AgNO <sub>3</sub> ] are the more important.
—	—	The sparing solubility of CaSO <sub>4</sub> (0.2 %) and comparative insolubility of SrSO <sub>4</sub> (0.01 %) is important in analysis.

Tables of Solubility (*continued*).

Class of Salts.	Solubility in water.	Solubility in Hydrochloric Acid.
8. Chlorides	All are soluble in water except <b>AgCl</b> , <b>HgCl</b> , <b>PbCl<sub>2</sub></b> , ( <b>Cu<sub>2</sub>Cl<sub>2</sub></b> ), and a few basic Chlorides, e. g. <b>SbOCl</b> and <b>BiOCl</b> . <b>PbCl<sub>2</sub></b> is moderately soluble in boiling water.	The basic Chlorides, e. g. <b>BiOCl</b> and <b>SbOCl</b> , are readily soluble, but many Chlorides easily soluble in water, e. g. <b>NaCl</b> , are insoluble in concentrated Hydrochloric Acid ( <b>Cu<sub>2</sub>Cl<sub>2</sub></b> is sol. in conc. <b>HCl</b> ).
9. Bromides	All are soluble in water except <b>AgBr</b> , <b>HgBr</b> , <b>PbBr<sub>2</sub></b> , (and <b>Cu<sub>2</sub>Br<sub>2</sub></b> ).	—
10. Iodides	All are soluble in water except <b>AgI</b> , <b>HgI</b> , <b>HgI<sub>2</sub></b> , <b>Cu<sub>2</sub>I<sub>2</sub></b> , <b>PbI<sub>2</sub></b> . <b>PbI<sub>2</sub></b> dissolves in boiling water.	<b>HCl</b> effects solution of <b>HgI<sub>2</sub></b> , which can be crystallized from that solvent.
11. Nitrates	All normal salts are soluble. A few basic salts, e. g. Bismuth Oxynitrate, <b>Bi(OH)<sub>2</sub>.NO<sub>3</sub></b> , are insoluble.	—
12. Phosphates	The normal and acid Phosphates of <b>Na</b> , <b>K</b> , and <b>NH<sub>4</sub></b> are soluble in water, and a few acid Phosphates, e. g. Superphosphate of Calcium, <b>Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub></b> , are slightly soluble. The others are insoluble.	All are soluble.
13. Arsenites	The Arsenites of <b>Na</b> , <b>K</b> , and <b>NH<sub>4</sub></b> are soluble in water. Most others are insoluble.	do.
14. Arsenates	The Arsenates of <b>Na</b> , <b>K</b> , and <b>NH<sub>4</sub></b> are soluble. Most others are insoluble.	do.
15. Oxalates	The Oxalates of <b>Na</b> , <b>K</b> , <b>NH<sub>4</sub></b> , (and <b>Cr</b> ) are soluble in water. Others are either slightly soluble or insoluble.	do.
16. Tartrates	The Tartrates of <b>Na</b> , <b>K</b> , and <b>NH<sub>4</sub></b> , and also Tartar Emetic, <b>K.SbO.C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.H<sub>2</sub>O</b> , are soluble in water. <b>KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub></b> is only sparingly soluble.	do.

Tables of Solubility (*continued*).

Solubility in Nitric Acid.	Solubility in Aqua Regia.	Remarks.
AgCl, HgCl, and PbCl <sub>2</sub> are hardly affected.	Mercurous Chloride, HgCl, would be dissolved to give HgCl <sub>2</sub> by the action of the nascent Chlorine.	AgCl is easily soluble in NH <sub>4</sub> OHAq. HgCl is blackened by NH <sub>4</sub> OHAq. PbCl <sub>2</sub> dissolves on boiling with water. Cuprous Chloride, Cu <sub>2</sub> Cl <sub>2</sub> , is a white solid which would rarely be met with in elementary analysis.
—	HgBr would be dissolved, forming HgCl <sub>2</sub> by the action of the nascent Chlorine.	AgBr dissolves with difficulty in NH <sub>4</sub> OHAq.
The Iodides insoluble in water are to some extent dissolved on boiling with HNO <sub>3</sub> with liberation of Iodine.	The Iodides insoluble in water would generally be dissolved as Chlorides with evolution of Iodine.	Insoluble Iodides are of characteristic colours:—AgI is faint yellow; HgI, fusch green; HgI <sub>2</sub> , scarlet; (Cu <sub>2</sub> I <sub>2</sub> , white); and PbI <sub>2</sub> , yellow.
The basic Nitrates dissolve readily on warming with dilute HNO <sub>3</sub> Aq.	—	The decomposition of the dry salt on heating to give brown fumes of NO <sub>2</sub> is often a valuable hint in analysis.
All are soluble.	All are soluble.	The insolubility of the Phosphates of the metals of Groups III, IV, V, and Mg in water, and their solubility in HClAq or HNO <sub>3</sub> Aq to give solutions from which NH <sub>4</sub> OHAq precipitates them, are of great importance in analysis (see p. 159).
do.	do.	The Arsenites of Na and K are the only common compounds.
do.	do.	The Arsenates of Na, K, (and Fe) are the only common compounds.
do.	do.	All decomposed on heating. Oxalates of Na and K give Carbonates on heating strongly—others generally give Oxides.
do.	do.	All decomposed on heating with charring, including the free acid.

## SUMMARY OF TESTS FOR ACID RADICLES.

The acids can be grouped in various ways, but for simplicity perhaps the following will be found most convenient:—

**Class I. Acids recognized on adding HClAq or H<sub>2</sub>SO<sub>4</sub>Aq to solid or concentrated solution (but preferably to solid) and warming gently.**

- (1) H<sub>2</sub>CO<sub>3</sub>.      (2) SH<sub>2</sub>.      (3) HCN.      (4) CH<sub>3</sub>COOH.  
 [(5) H<sub>2</sub>SO<sub>3</sub>.]      [(6) HNO<sub>2</sub>.]

**Class II. Acids readily recognized in strongly acid solution by addition of (a) Ba(NO<sub>3</sub>)<sub>2</sub>Aq (or BaCl<sub>2</sub>Aq), (b) AgNO<sub>3</sub>Aq.**

- (7) H<sub>2</sub>SO<sub>4</sub>.      (8) HCl.      (9) HBr.      (10) HI.

**Class III. Acids for which special tests must be made in strongly acid solution.**

- (11) HNO<sub>3</sub>.      (12) H<sub>3</sub>PO<sub>4</sub>.

**Class IV. Acids detected in neutral solution by addition of (a) CaCl<sub>2</sub>Aq, (b) AgNO<sub>3</sub>Aq.**

- (13) H<sub>3</sub>AsO<sub>3</sub>.      (14) H<sub>3</sub>AsO<sub>4</sub>.      (15) H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.  
 (16) H<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.

# REACTIONS OF SALTS OF THE ACIDS, WITH TESTS FOR FREE ACIDS, WHERE MET WITH.

## (1) CARBONATES.

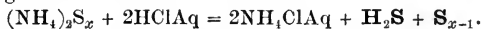
Reagent.	Result observed.	Remarks.
1. HClAq or H <sub>2</sub> SO <sub>4</sub> Gas evolved is tested by lime-water.	All Carbonates are decomposed by addition of acids to the solution and gentle warming. e. g. BaCO <sub>3</sub> + 2HClAq = BaCl <sub>2</sub> Aq + H <sub>2</sub> O + CO <sub>2</sub> If the Carbon Dioxide is passed into lime-water a white precipitate of Calcium Carbonate will be thrown down. CO <sub>2</sub> + Ca(OH) <sub>2</sub> = CaCO <sub>3</sub> + H <sub>2</sub> O	A Carbonate would probably be attacked on testing for Group I of the metals, or on trying to dissolve the substance in acid.
2. CaCl <sub>2</sub> or AgNO <sub>3</sub>	If the Carbonate is soluble in water the precipitation of insoluble Carbonates could be used as a test, e. g. precipitation of CaCO <sub>3</sub> and Ag <sub>2</sub> CO <sub>3</sub> . e. g. (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> Aq + CaCl <sub>2</sub> Aq = CaCO <sub>3</sub> + 2NH <sub>4</sub> ClAq Na <sub>2</sub> CO <sub>3</sub> Aq + 2AgNO <sub>3</sub> Aq = Ag <sub>2</sub> CO <sub>3</sub> + 2NaNO <sub>3</sub> Aq	This test is only applicable to Carbonates of Na, K, or NH <sub>4</sub> .  (The free acid could only be met with in dilute solution, e. g. in soda water.)

## (2) SULPHIDES (AND SULPHURETTED HYDROGEN).

Reagent.	Result observed.	Remarks.
1. HCl	H <sub>2</sub> S is evolved, <sup>1</sup> and can be recognized by its odour, and by the blackening of a piece of filter paper moistened with a solution of a Lead salt, e. g. Lead Acetate. $\text{FeS} + 2\text{HClAq} = \text{FeCl}_2\text{Aq} + \text{H}_2\text{S}$ $(\text{CH}_3\text{.COO})_2\text{Pb} + \text{H}_2\text{S} = \text{PbS} + 2\text{CH}_3\text{.COOH}$	
2. AgNO <sub>3</sub> (CH <sub>3</sub> .COO) <sub>2</sub> Pb or CuSO <sub>4</sub> for soluble Sulphides.	Soluble Sulphides cause the formation of characteristic precipitates with salts of metals which form insoluble Sulphides. e. g. (NH <sub>4</sub> ) <sub>2</sub> SAq + 2AgNO <sub>3</sub> Aq $= \text{Ag}_2\text{S} + 2\text{NH}_4\text{NO}_3$	This test would only apply to the Sulphides of Na, K, NH <sub>4</sub> , or to the free acid in solution H <sub>2</sub> SAq.

<sup>1</sup> Special Notes on Sulphides.

(1) With polysulphides, HClAq sets free SH<sub>2</sub> and precipitates Sulphur as a nearly white precipitate, e. g.



(2) A few Sulphides are practically insoluble unless in HNO<sub>3</sub>Aq or Aqua regia, e. g. As<sub>2</sub>S<sub>3</sub>, HgS, and FeS<sub>2</sub>. Aqua regia, using minimum quantity of Nitric Acid, may cause evolution of enough H<sub>2</sub>S to blacken Lead Acetate paper. The Sulphur present is, however, chiefly converted into H<sub>2</sub>SO<sub>4</sub>, which, if tested for with BaCl<sub>2</sub>Aq and found, would, taking into account the physical properties of the body, be regarded as confirming Sulphide.

## (Free Acid.

(3) The free acid, Hydrogen Sulphide, would be readily detected by its odour and reactions with the metals of Groups I and II. No residue would be left on evaporation of Sulphuretted Hydrogen solution to dryness.)

## (3) CYANIDES AND HYDROCYANIC ACID.

Reagent.	Result observed.	Remarks.
1. $\text{HCl}$ or $\text{H}_2\text{SO}_4$	HCN is evolved on warming gently. The odour is characteristic. e.g. $\text{KCNAq} + \text{HClAq} = \text{KClAq} + \text{HCN}$	The acid itself and the Alkali Cyanides NaCN and KCN have the characteristic odour of bitter almonds. Some have difficulty in detecting this odour. A student should find out whether he can recognize it both because the acid is poisonous and for analytical reasons.
2. Prussian Blue Test. $\text{FeSO}_4 \cdot \text{NaOH}$ $\text{FeCl}_3 \cdot \text{HCl}$	Add $\text{FeSO}_4\text{Aq}$ and $\text{NaOHAq}$ and warm gently, then add two or three drops of $\text{FeCl}_3\text{Aq}$ and enough $\text{HClAq}$ to dissolve any hydroxides which may have precipitated. A deep blue precipitate—Prussian blue—is thrown down. The following equations explain the different stages of the reaction: $\begin{aligned} a) \text{FeSO}_4\text{Aq} + 2\text{NaOHAq} &= \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4\text{Aq} \\ b) 6\text{KCNAq} + \text{Fe(OH)}_2 &= \text{K}_4\text{Fe(CN)}_6\text{Aq} + 2\text{KOHAq} \\ c) 3\text{K}_4\text{Fe(CN)}_6\text{Aq} + 4\text{FeCl}_3\text{Aq} &= \text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{KClAq} \end{aligned}$	
3. Sulpho-cyanide Test.	Evaporate a few c.c. of the Cyanide solution with two or three drops of yellow Ammonium Sulphide in a porcelain basin on a water-bath to dryness; then add a drop of dil. $\text{HCl}$ and a couple of drops of $\text{FeCl}_3\text{Aq}$ . An intense red coloration will be obtained. On warming a Cyanide with Ammonium Sulphide, Ammonium Sulphocyanide is formed, and this substance with $\text{FeCl}_3\text{Aq}$ gives Ferric Sulphocyanide (thiocyanate) which is red. $\text{FeCl}_3\text{Aq} + 3\text{NH}_4\text{SCNAq} = \text{Fe(SCN)}_3 + 3\text{NH}_4\text{ClAq}$	

## Tests for free Acid.

The free acid  $\text{HCNAq}$  (a) would have odour of bitter almonds, (b) would give above tests, and (c) would yield no residue on evaporation to dryness.



## (4) ACETATES AND ACETIC ACID.

Reagent.	Result observed.	Remarks.
1. $\text{HCl}$ or $\text{H}_2\text{SO}_4$	On heating the solid or a concentrated solution with $\text{HCl}$ (or $\text{H}_2\text{SO}_4$ ), Acetic Acid is liberated, and on warming the odour of vinegar can generally be noted. (If in doubt compare with odour of Acetic Acid solution on reagent bench.) e.g. $\text{CH}_3\text{COONa} + \text{HClAq}$ $\quad\quad\quad = \text{CH}_3\cdot\text{COOH} + \text{NaClAq}$	If solid Acetates are rubbed between the fingers, the odour of vinegar can sometimes be detected.
2. $\text{FeCl}_3$	With neutral solutions of Acetates $\text{FeCl}_3\text{Aq}$ gives a red colour due to formation of <b>Ferric Acetate</b> in solution, and on boiling a brown precipitate of <b>Basic Ferric Acetate</b> is thrown down. a) $3\text{CH}_3\text{COONaAq} + \text{FeCl}_3\text{Aq}$ $\quad\quad\quad = (\text{CH}_3\cdot\text{COO})_3\text{Fe} + 3\text{NaClAq}$ b) $(\text{CH}_3\text{COO})_3\text{Fe} + 2\text{H}_2\text{O}$ $\quad\quad\quad = \text{Fe}(\text{OH})_2(\text{CH}_3\text{COO}) + 2\text{CH}_3\text{COOH}$ $\quad\quad\quad \text{Basic Ferric Acetate}$	
3. $\text{C}_2\text{H}_5\text{OH}$ and $\text{H}_2\text{SO}_4$	Add a few drops of alcohol to very conc. solution, or preferably to solid, then add conc. $\text{H}_2\text{SO}_4$ and warm gently. Ethyl Acetate is formed and can be recognized by its pleasant fruity odour. a) $\text{CH}_3\text{COONa} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{CH}_3\text{COOH}$ b) $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$ $\quad\quad\quad = \text{CH}_3\cdot\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ $\quad\quad\quad \text{Ethyl Acetate}$	The odour of Ethyl Acetate must be carefully distinguished from that of Ethyl Ether, which might be produced from the alcohol and Sulphuric Acid alone.

## Tests for free Acid.

The free acid would (a) smell of vinegar, and (b) on evaporation to dryness would leave no residue. (c) Above tests could be obtained if the acid were neutralized with  $\text{NaOHAq}$  and evaporated down.

## (5) SULPHITES AND SULPHUROUS ACID.

Reagent.	Result observed.	Remarks.
1. $\text{HCl}$ or $\text{H}_2\text{SO}_4$	Sulphurous Acid is liberated, which splits up to form $\text{SO}_2$ and water. The Sulphur Dioxide is readily detected by its odour on warming the solution. e. g. $\text{Na}_2\text{SO}_3\text{Aq} + 2\text{HClAq} = 2\text{NaClAq} + \text{H}_2\text{O} + \text{SO}_2$	The pure acid is unknown, but a solution which smells strongly of $\text{SO}_2$ is readily obtained by passing $\text{SO}_2$ into water. No residue is left on evaporation to dryness.
2. $\text{BaCl}_2$	A white precipitate of Barium Sulphite, $\text{BaSO}_3$ , is obtained, soluble in $\text{HClAq}$ . e. g. $\text{Na}_2\text{SO}_3\text{Aq} + \text{BaCl}_2\text{Aq} = \text{BaSO}_3 + 2\text{NaClAq}$	The solubility of the precipitate in $\text{HCl}$ is rarely complete because Sulphites are generally contaminated with Sulphates produced by the action of the oxygen of the air.
3. $\text{AgNO}_3$	A white precipitate of Silver Sulphite is obtained, soluble in hot dil. $\text{HNO}_3$ . e. g. $\text{Na}_2\text{SO}_3\text{Aq} + 2\text{AgNO}_3\text{Aq} = \text{Ag}_2\text{SO}_3 + 2\text{NaNO}_3\text{Aq}$ Silver Sulphite is decomposed on boiling, turning grey owing to the deposition of Silver, Silver Sulphate being also formed. $2\text{Ag}_2\text{SO}_3 = 2\text{Ag} + \text{Ag}_2\text{SO}_4 + \text{SO}_2$	
4. Decolorization of $\text{KMnO}_4\text{Aq}$	An acidified solution of a Sulphite readily decolorizes Potassium Permanganate because of the transformation of Sulphur Dioxide to Sulphur Trioxide. $2\text{KMnO}_4 + 5\text{H}_2\text{SO}_3\text{Aq} = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 2\text{H}_2\text{SO}_4$	
5. $\text{K}_2\text{Cr}_2\text{O}_7$	Solutions of Chromates and Dichromates are turned green if added to an acidified solution of a Sulphite. $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 3\text{H}_2\text{SO}_3 = \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O}$	
6. Carbon and $\text{Na}_2\text{CO}_3$	On heating a Sulphide with $\text{Na}_2\text{CO}_3$ on charcoal Sodium Sulphide is formed, which can be detected by placing a little of the fused mass on a silver coin and moistening with water. A black stain is formed.	

## (6) NITRITES.

Reagent.	Result observed.	Remarks.
1. $\text{HCl}$ or $\text{H}_2\text{SO}_4$	Nitrites are decomposed, giving Nitric Oxide, $\text{NO}$ , and Nitric Peroxide, $\text{NO}_2$ . e. g. a) $\text{NaNO}_2 + \text{HClAq} = \text{NaClAq} + \text{HNO}_2$ b) $3\text{HNO}_2 = \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$ c) $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ from air	The free acid is not met with. Even a dilute solution splits up at ordinary temp. as indicated in equation b.
2. $\text{FeSO}_4\text{Aq}$ and acid	A solution of Ferrous Sulphate with a few drops of Acetic Acid gives a deep brown solution of $\text{NO} \cdot 2\text{FeSO}_4\text{Aq}$ (brown ring). a) $\text{NaNO}_2 + \text{CH}_3\text{COOHAq} = \text{CH}_3\text{COONa} + \text{HNO}_2$ b) $3\text{HNO}_2 = \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$ c) $\text{NO} + 2\text{FeSO}_4\text{Aq} = \text{NO} \cdot 2\text{FeSO}_4$	
3. $\text{AgNO}_3$	With a concentrated solution of a nitrite, a white precipitate of Silver Nitrite is thrown down. e. g. $\text{NaNO}_2\text{Aq} + \text{AgNO}_3\text{Aq}$ $\quad\quad\quad = \text{AgNO}_2 + \text{NaNO}_3\text{Aq}$	
4. $\text{KI}$ , $\text{H}_2\text{SO}_4$ and starch	On adding $\text{KIAq}$ , starch solution, and dilute Sulphuric Acid to a solution of a Nitrite, a deep blue coloration is obtained, due to the formation of Starch Iodide. e. g. a) $\text{NaNO}_2\text{Aq} + \text{H}_2\text{SO}_4\text{Aq}$ $\quad\quad\quad = \text{NaHSO}_4\text{Aq} + \text{HNO}_2\text{Aq}$ b) $\text{KIAq} + \text{H}_2\text{SO}_4\text{Aq} = \text{KHSO}_4\text{Aq} + \text{HIAq}$ c) $2\text{HIAq} + 2\text{HNO}_2\text{Aq} = 2\text{H}_2\text{O} + \text{I}_2 + 2\text{NO}$ The Iodine and Starch form Starch Iodide.	

## (7) SULPHATES AND SULPHURIC ACID.

Reagent.	Result observed.	Remarks.
1. $\text{BaCl}_2$	A white precipitate of Barium Sulphate, $\text{BaSO}_4$ , is obtained, insoluble in acids. e. g. $\text{CuSO}_4\text{Aq} + \text{BaCl}_2\text{Aq} = \text{BaSO}_4 + \text{CuCl}_2\text{Aq}$	
2. $(\text{CH}_3\text{COO})_2\text{Pb}$	A white precipitate of Lead Sulphate, $\text{PbSO}_4$ , is thrown down. The precipitate is soluble with difficulty in Ammonium Acetate and in Potash. $\text{Na}_2\text{SO}_4\text{Aq} + (\text{CH}_3\text{COO})_2\text{PbAq}$ $\quad\quad\quad = \text{PbSO}_4 + 2\text{CH}_3\cdot\text{COONa}$	
3. Dry Test. Carbon and $\text{Na}_2\text{CO}_3$	Heated on charcoal with $\text{Na}_2\text{CO}_3$ all Sulphates give Sulphide. e. g. $\text{BaSO}_4 + 2\text{C} + \text{Na}_2\text{CO}_3$ $\quad\quad\quad = \text{BaS} + \text{BaCO}_3 + 2\text{CO}_2$ On putting a little of the fused mass (after cooling) on a silver coin and moistening with water, a black stain is produced, due to formation of $\text{Ag}_2\text{S}$ .	Sulphites give a similar reaction (p. 194).

## Special Tests for free Sulphuric Acid in Solution.

(The pure free acid is an oily liquid, sp. gr. 1.85.)

(1) The reaction would be strongly acid. (**Note.**— $\text{NaHSO}_4$  and  $\text{KHSO}_4$  would also be strongly acid.)(2) On evaporating a solution of Sulphuric Acid a few drops of an oily liquid would be obtained which would dissociate into  $\text{SO}_3$  and  $\text{H}_2\text{O}$ , dense white choking fumes being evolved.

(3) The hot concentrated solution would immediately char organic substances, e. g. filter paper, starch, &amp;c.

(4) The solution would give above tests with  $\text{BaCl}_2$  and  $(\text{CH}_3\cdot\text{COO})_2\text{Pb}$ .

## (8) CHLORIDES AND HYDROCHLORIC ACID.

Reagent.	Result observed.	Remarks.
1. $\text{AgNO}_3$	A white curdy precipitate of Silver Chloride, $\text{AgCl}$ , is obtained, easily soluble in $\text{NH}_4\text{OHAq}$ , insoluble in Nitric Acid. e. g. $\text{CaCl}_2\text{Aq} + 2\text{AgNO}_3\text{Aq}$ $\quad\quad\quad = 2\text{AgCl} + \text{Ca}(\text{NO}_3)_2\text{Aq}$	
2. $\text{Cl}_2\text{Aq}$ , Chlorine water	No action (cf. Bromides and Iodides).	
3. $\text{MnO}_2$ and $\text{H}_2\text{SO}_4$ (concentrated)	On addition of $\text{MnO}_2$ and conc. $\text{H}_2\text{SO}_4$ to solid subs. or concentrated solution, Chlorine gas is evolved and recognized by colour, odour, and bleaching action on moist litmus paper. Warm gently if necessary. e. g. $\text{CaCl}_2 + \text{MnO}_2 + 2\text{H}_2\text{SO}_4$ $\quad\quad\quad = \text{ZnSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$ The bleaching action depends upon the formation of nascent oxygen. $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \text{O}$	<b>Caution.</b> Do not add conc. $\text{H}_2\text{SO}_4$ to a hot solution.
4. $\text{H}_2\text{SO}_4$ (concentrated)	With conc. solution or solid, $\text{HCl}$ is evolved as a fuming gas with pungent odour. It gives dense white fumes when a rod moistened with Ammonia solution is brought over the test-tube. e. g. $\text{NaCl} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HCl}$ $\text{HCl} + \text{NH}_3 = \text{NH}_4\text{Cl}$	
5. $(\text{CH}_3\text{COO})_2\text{Pb}$	White precipitate of Lead Chloride ( $\text{PbCl}_2$ ), which can be recrystallized from boiling water in characteristic crystals. e. g. $\text{CaCl}_2\text{Aq} + (\text{CH}_3\text{COO})_2\text{PbAq}$ $\quad\quad\quad = \text{PbCl}_2 + (\text{CH}_3\text{COO})_2\text{CaAq}$ <div style="text-align: center;">Calcium Acetate</div>	

**Special Tests for free HCl in Solution.**

Free Hydrochloric Acid solution would give above tests and also the following :—

(1) It would be strongly acid in reaction.

(2) No residue would be left on evaporation if the free acid alone were present. During evaporation pungent acid fumes would be evolved, which would give dense white fumes with a drop of Ammonia solution held over the evaporating basin on a glass rod.

## (9) BROMIDES AND HYDROBROMIC ACID.

Reagent.	Result observed.	Remarks.
1. $\text{AgNO}_3$	A faintly yellow precipitate of Silver Bromide comes down, insoluble in $\text{HNO}_3\text{Aq}$ , but <b>soluble with difficulty in <math>\text{NH}_4\text{OHAq}</math>.</b> $\text{KBrAq} + \text{AgNO}_3\text{Aq} = \text{AgBr} + \text{KNO}_3\text{Aq}$	Cf. HCl and HI.
2. $\text{Cl}_2\text{Aq}$ , Chlorine water	Bromine is liberated, which colours the liquid brown. $2\text{KBrAq} + \text{Cl}_2\text{Aq} = 2\text{KClAq} + \text{Br}_2\text{Aq}$ On shaking with Carbon Disulphide, $\text{CS}_2$ , or Chloroform, $\text{CHCl}_3$ , the Bromine dissolves to give a brown solution of Bromine in $\text{CS}_2$ or $\text{CHCl}_3$ at the bottom of the test-tube.	Large excess of Chlorine water will discharge the colour, oxidizing the Bromine to Bromic Acid.
3. $\text{MnO}_2$ and $\text{H}_2\text{SO}_4$ (concentrated)	On addition of $\text{MnO}_2$ and conc. $\text{H}_2\text{SO}_4$ to solid substance or concentrated solution, Bromine, readily recognized by its colour and pungent odour, is set free. e. g. $2\text{KBr} + \text{MnO}_2 + \text{H}_2\text{SO}_4$ $= \text{Br}_2 + \text{K}_2\text{SO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O}$	<b>Caution.</b> Do not add conc. $\text{H}_2\text{SO}_4$ to a hot solution.
4. $\text{H}_2\text{SO}_4$ (concentrated)	On addition of conc. $\text{H}_2\text{SO}_4$ to solid or concentrated solution, Hydrobromic Acid is evolved as a fuming gas with pungent odour, but Bromine is always given off at the same time, because of the oxidizing action of the Sulphuric Acid on the HBr. a) $\text{KBr} + \text{H}_2\text{SO}_4 = \text{KHSO}_4 + \text{HBr}$ b) $2\text{HBr} + \text{H}_2\text{SO}_4 = 2\text{H}_2\text{O} + \text{Br}_2 + \text{SO}_2$	
5. $(\text{CH}_3\text{COO})_2\text{Pb}$	Lead Acetate gives a white precipitate of Lead Bromide, which can be recrystallized from boiling water. $2\text{NaBrAq} + (\text{CH}_3\text{COO})_2\text{PbAq}$ $= \text{PbBr}_2 + 2\text{CH}_3\text{COONaAq}$	

**Note.**—Free Hydrobromic Acid Solution would not readily be met with. It is similar in properties to Hydrochloric Acid, HCl.

## (10) IODIDES AND HYDRIODIC ACID.

Reagent.	Result observed.	Remarks.
1. $\text{AgNO}_3$	A light yellow precipitate of Silver Iodide, $\text{AgI}$ , comes down, insoluble in $\text{HNO}_3\text{Aq}$ and in $\text{NH}_4\text{OHAq}$ . $2\text{KIAq} + \text{AgNO}_3\text{Aq} = \text{AgI} + \text{KNO}_3\text{Aq}$	Cf. $\text{HCl}$ and $\text{HBr}$ .
2. $\text{Cl}_2\text{Aq}$ , Chlorine water	Iodine is liberated, forming a brown solution. On shaking with $\text{CS}_2$ or $\text{CHCl}_3$ the Iodine dissolves to give a violet solution of Iodine in $\text{CS}_2$ or $\text{CHCl}_3$ at the bottom of the tube. $2\text{KIAq} + \text{Cl}_2\text{Aq} = 2\text{KClAq} + \text{I}_2$	Large excess of Chlorine water will discharge the colour, oxidizing the Iodine to Iodic Acid. $\text{I}_2 + 5\text{Cl}_2 + 6\text{H}_2\text{O} = 2\text{HIO}_3 + 10\text{HCl}$ Iodic Acid
3. $\text{MnO}_2$ and $\text{H}_2\text{SO}_4$ (concentrated)	With solid substance or concentrated solution, Iodine vapour of characteristic violet colour is set free. The Iodine may condense on the upper portion of the tube in glistening grey crystals. $2\text{KI} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{I}_2$	Cf. $\text{HBr}$ .
4. $\text{H}_2\text{SO}_4$ (concentrated)	With concentrated solution or solid, $\text{HI}$ is evolved as fuming gas with pungent odour, but Iodine is always given off at the same time. a) $2\text{KI} + \text{H}_2\text{SO}_4 = 2\text{HI} + \text{K}_2\text{SO}_4$ b) $2\text{HI} + \text{H}_2\text{SO}_4 = \text{I}_2 + 2\text{H}_2\text{O} + \text{SO}_2$	
5. $\text{HgCl}_2$	A scarlet precipitate of Mercuric Iodide, $\text{HgI}_2$ , is obtained. $2\text{KIAq} + \text{HgCl}_2\text{Aq} = \text{HgI}_2 + 2\text{KClAq}$	
6. $(\text{CH}_3\text{COO})_2\text{Pb}$	A yellow precipitate of Lead Iodide, $\text{PbI}_2$ , forms. $2\text{KIAq} + (\text{CH}_3\text{COO})_2\text{PbAq} = \text{PbI}_2 + 2\text{CH}_3\text{COOKAq}$	

**Note.**—Free Hydriodic Acid solution is rarely met with in Analysis. It is similar in properties to  $\text{HClAq}$  and  $\text{HBrAq}$ , but is generally coloured brown from presence of free Iodine.

## (11) NITRATES AND NITRIC ACID.

Reagent.	Result observed.	Remarks.
1. $\text{H}_2\text{SO}_4$ (concentrated) and Cu turnings	<p>Add to concentrated solution an equal bulk of conc. <math>\text{H}_2\text{SO}_4</math>, and then a few pieces of Cu turnings: brown fumes of <math>\text{NO}_2</math> are evolved, and a blue solution is formed. <math>\text{HNO}_3</math> is first liberated, which reacts with the Copper to give Copper Nitrate with evolution of <math>\text{NO}</math>. The oxygen of the air in the tube causes formation of brown fumes of <math>\text{NO}_2</math>.</p> <p>e.g. <math>\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HNO}_3</math>  <math>3\text{Cu} + 8\text{HNO}_3\text{Aq} = 3\text{Cu}(\text{NO}_3)_2\text{Aq} + 4\text{H}_2\text{O} + 2\text{NO}</math>  <math>2\text{NO} + \text{O}_2 = 2\text{NO}_2</math></p>	Warm if necessary.
2. Brown Ring Test. $\text{H}_2\text{SO}_4$ and $\text{FeSO}_4$	<p>There are various methods of carrying out this test. The following is probably the most delicate: Add to conc. solution rather less than equal bulk of conc. <math>\text{H}_2\text{SO}_4</math>, cool well, and then pour carefully down the side of the tube so as to form an upper layer a freshly prepared cold solution of Ferrous Sulphate, <math>\text{FeSO}_4</math>. A brown ring or band is produced at the junction of the liquids by the formation of an unstable double compound of Nitric Oxide and <math>\text{FeSO}_4</math>, which has the composition <math>\text{NO} \cdot 2\text{FeSO}_4</math> at ordinary temperatures (p. 31). The Sulphuric Acid in the first instance sets free Nitric Acid, which oxidizes part of the Ferrous Sulphate to Ferric Sulphate with separation of <math>\text{NO}</math>, which combines with unaltered <math>\text{FeSO}_4</math> to give the brown ring.</p> <p>e.g. a) <math>\text{KNO}_3\text{Aq} + \text{H}_2\text{SO}_4 = \text{KHSO}_4\text{Aq} + \text{HNO}_3\text{Aq}</math>  b) <math>6\text{FeSO}_4\text{Aq} + 3\text{H}_2\text{SO}_4 + 2\text{HNO}_3\text{Aq} = 3\text{Fe}_2(\text{SO}_4)_3\text{Aq} + 4\text{H}_2\text{O} + 2\text{NO}</math>  c) <math>2\text{FeSO}_4 + \text{NO} = \text{NO} \cdot 2\text{FeSO}_4</math></p> <p>Note.—A quicker but less reliable method of carrying out this test is to add a crystal of Ferrous Sulphate to the original conc. solution and then conc. Sulphuric Acid. A brownish black coloration appears round the crystal.</p>	<p>The brown ring test must be used with great caution if Bromide or Iodide be present, as, under the conditions of the experiment, rings of Bromine or Iodine may be produced which simulate the brown ring.</p> <p>In the presence of Nitrites the test is valueless.</p>
3. Charcoal.	On heating Nitrates on charcoal they generally deflagrate.	
4. Heat solid in dry tube.	On heating in dry tube of hard glass Nitrates decompose, giving off brown fumes.	

## Special Tests for Free Nitric Acid.

Free  $\text{HNO}_3\text{Aq}$  would be strongly acid in reaction, would give above reactions easily, and leave no residue on evaporation. Towards the end of the evaporation acid fumes would be evolved with pungent odour, and at this stage a few pieces of Copper foil added would cause immediate evolution of brown fumes.



## (12) PHOSPHORIC ACID AND PHOSPHATES.

Reagent.	Result observed.	Remarks.
1. $(\text{NH}_4)_2\text{MoO}_4$ and $\text{HNO}_3$	<b>Ammonium Nitromolybdate Test.</b> Add to 2-3 c.c. of solution of subs.—dissolved in water or in $\text{HNO}_3\text{Aq}$ —about double the volume of Ammonium Nitromolybdate (i.e. Ammon. Molybdate and $\text{HNO}_3$ ) and warm gently. A yellow coloration and finally a canary yellow precipitate of Ammonium Phosphomolybdate indicates Phosphoric Acid. The precipitate is of complicated constitution, $11\text{MoO}_3 \cdot (\text{NH}_4)_3\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , and no satisfactory simple equation can be given.	Arsenates may give a similar precipitate on boiling.
2. $\text{AgNO}_3$	In neutral solutions Phosphates give a yellow precipitate of Silver Phosphate, $\text{Ag}_3\text{PO}_4$ . $3\text{Na}_2\text{HPO}_4\text{Aq} + 6\text{AgNO}_3\text{Aq}$ $= 2\text{Ag}_3\text{PO}_4 + 6\text{NaNO}_3\text{Aq} + \text{H}_3\text{PO}_4\text{Aq}$	The precipitate is exactly similar in appearance to Silver Arsenite.
3. Magnesia mixture, $\text{MgSO}_4$ , $\text{NH}_4\text{Cl}$ , and $\text{NH}_4\text{OH}$	On addition of $\text{NH}_4\text{ClAq}$ , $\text{NH}_4\text{OHAq}$ , and $\text{MgSO}_4\text{Aq}$ to solution of a Phosphate a white precipitate of Magnesium Ammonium Phosphate may be obtained. e.g. $\text{Na}_2\text{HPO}_4\text{Aq} + \text{NH}_4\text{OHAq} + \text{MgSO}_4\text{Aq}$ $= \text{Mg} \cdot \text{NH}_4\text{PO}_4 + \text{Na}_2\text{SO}_4\text{Aq}$	The $\text{NH}_4\text{Cl}$ is added to prevent precipitation of Magnesium Hydroxide by $\text{NH}_4\text{OHAq}$ .
4. $\text{CaCl}_2$ or $\text{BaCl}_2$	White precipitates of Calcium and Barium Phosphates soluble in Acetic and in Mineral Acids are obtained. e.g. $\text{Na}_2\text{HPO}_4\text{Aq} + \text{CaCl}_2\text{Aq}$ $= \text{CaHPO}_4 + 2\text{NaClAq}$	$\text{Ca}_3(\text{PO}_4)_2$ would also be precipitated.
5. $\text{FeCl}_3$	A yellowish white precipitate of Ferric Phosphate is obtained which is soluble in Mineral Acids, but not in Acetic Acid. [This reaction is of special importance because it is used in quantitatively separating Phosphoric Acid from solution. In order to make the reaction quantitative Ammonium or Sodium Acetate should be added to the solution to prevent free $\text{HCl}$ being formed during the reaction (see p. 159).] $\text{Na}_2\text{HPO}_4\text{Aq} + \text{FeCl}_3\text{Aq}$ $= \text{FePO}_4 + 2\text{NaClAq} + \text{HClAq}$ $\text{HCl} + \text{CH}_3 \cdot \text{COONaAq}$ $= \text{NaClAq} + \text{CH}_3 \cdot \text{COOH}$	

## (13) ARSENITES AND ARSENIOS ACID.

Reagent.	Result observed.	Remarks.
1. $\text{SH}_2$ (in presence of $\text{HCl}$ )	A yellow precipitate of Arsenious Sulphide, $\text{As}_2\text{S}_3$ , is thrown down. The solution must be acid as the precipitate is soluble in $\text{NaOHAq}$ or $\text{KOH Aq}$ . (See p. 106.) $2\text{H}_3\text{AsO}_3\text{Aq} + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 6\text{H}_2\text{O}$	
2. $\text{AgNO}_3$	With neutral solutions a yellow precipitate of Silver Arsenite, $\text{Ag}_3\text{AsO}_3$ , comes down. The precipitate is soluble in acids and in $\text{NH}_4\text{OHAq}$ . $\text{Na}_3\text{AsO}_3\text{Aq} + 3\text{AgNO}_3\text{Aq} = \text{Ag}_3\text{AsO}_3 + 3\text{NaNO}_3\text{Aq}$	Cf. $\text{Ag}_3\text{PO}_4$ above (p. 201).
3. $(\text{CH}_3\text{COO})_2\text{Pb}$	White precipitate of Lead Arsenite, soluble in Acetic Acid, forms. $2\text{Na}_3\text{AsO}_3\text{Aq} + 3(\text{CH}_3\text{COO})_2\text{PbAq} = 6\text{CH}_3\text{COOKAq} + \text{Pb}_3(\text{AsO}_3)_2$	
4. Iodine in $\text{KIAq}$	The solution is decolorized owing to oxidation of the Arsenite to Arsenate. $\text{H}_3\text{AsO}_3\text{Aq} + \text{I}_2 + \text{H}_2\text{O} = \text{H}_3\text{AsO}_4\text{Aq} + 2\text{HIAq}$	

## (14) ARSENATES AND ARSENIC ACID.

Reagent.	Result observed.	Remarks.
1. $\text{SH}_2$	On passing gaseous $\text{SH}_2$ through a solution of an Arsenate, reduction to Arsenite <b>slowly</b> takes place, and afterwards a precipitate of Arsenious Sulphide forms. $a) \text{H}_3\text{AsO}_4 + \text{H}_2\text{S} = \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} + \text{S}.$ $b) 2\text{H}_3\text{AsO}_3 + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 6\text{H}_2\text{O}.$	
2. $\text{H}_2\text{SO}_3\text{Aq}$	Rapid reduction of Arsenate to Arsenite takes place, and after boiling off any excess of Sulphur Dioxide, the solution will give a precipitate with $\text{SH}_2$ . $\text{H}_3\text{AsO}_4\text{Aq} + \text{H}_2\text{SO}_3\text{Aq} = \text{H}_3\text{AsO}_3\text{Aq} + \text{H}_2\text{SO}_4\text{Aq}$ <div style="display: flex; justify-content: space-around; width: 100%;"> <span>Arsenic Acid</span> <span>Arsenious Acid</span> </div>	
3. $\text{AgNO}_3$	With neutral solutions a reddish brown precipitate of Silver Arsenate forms, soluble in acids and in $\text{NH}_4\text{OHAq}$ . $3\text{Na}_2\text{HAsO}_4\text{Aq} + 6\text{AgNO}_3\text{Aq}$ $= 2\text{Ag}_3\text{AsO}_4 + 6\text{NaNO}_3\text{Aq} + \text{H}_3\text{AsO}_4\text{Aq}$	The precipitate would not form immediately in presence of Chlorides, Bromides, and Iodides, and would not appear if solution were strongly acid.
4. <b>Magnesia mixture,</b> $\text{MgSO}_4$ , $\text{NH}_4\text{Cl}$ , and $\text{NH}_4\text{OH}$	From neutral or alkaline solutions of Arsenates a white precipitate of Magnesium Ammon. Arsenate is obtained. $\text{Na}_2\text{HAsO}_4\text{Aq} + \text{MgSO}_4\text{Aq} + \text{NH}_4\text{OHAq}$ $= \text{MgNH}_4\text{AsO}_4 + \text{Na}_2\text{SO}_4\text{Aq} + \text{H}_2\text{O}$	
5. $(\text{CH}_3\text{COO})_2\text{Pb}$	A white precipitate of Lead Arsenate insoluble in Acetic Acid comes down. $2\text{Na}_2\text{HAsO}_4 + 3(\text{CH}_3\text{COO})_2\text{Pb}$ $= \text{Pb}_3(\text{AsO}_4)_2 + 2\text{CH}_3\text{COOKAq} + 2\text{CH}_3\text{COOH}$	

## (15) OXALATES AND OXALIC ACID.

Reagent.	Result observed.	Remarks.
1. Heat dry substance	The acid itself partly sublimes and partly decomposes (see below); the oxalates of the metals decompose with only slight charring as a rule, to give <b>Carbonates</b> . On strong ignition <b>Oxides</b> would be obtained, except in case of Oxalates of Na and K.	
2. $\text{H}_2\text{SO}_4$ (concentrated)	On warming Oxalic Acid and Oxalates with concentrated $\text{H}_2\text{SO}_4$ , evolution of CO and $\text{CO}_2$ takes place with very slight charring as a rule. The Carbon Monoxide, CO, can generally be burnt at the mouth of the tube. e. g. $\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 = \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{CO} + \text{CO}_2$ $\text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO} + \text{CO}_2$	
3. $\text{CaCl}_2$	With neutral solutions of Oxalates a white precipitate of <b>Calcium Oxalate</b> is obtained, insoluble in Acetic Acid. $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq} + \text{CaCl}_2\text{Aq} = \text{CaC}_2\text{O}_4 + 2\text{NH}_4\text{ClAq}$ If the precipitate is filtered off and a little of it carefully heated on a spatula in the Bunsen flame, Calcium Carbonate is formed. On addition of a drop of HCl this residue would effervesce, giving off $\text{CO}_2$ , whereas the original precipitate would not do so. $\text{CaC}_2\text{O}_4 = \text{CaCO}_3 + \text{CO} + \text{CO}_2$	
4. $\text{AgNO}_3$	A white precipitate of Silver Oxalate, soluble in $\text{HNO}_3\text{Aq}$ and $\text{NH}_4\text{OHAq}$ , forms. $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq} + 2\text{AgNO}_3\text{Aq} = \text{Ag}_2\text{C}_2\text{O}_4 + 2\text{NH}_4\text{NO}_3\text{Aq}$	
5. $\text{KMnO}_4$ and $\text{H}_2\text{SO}_4\text{Aq}$	On adding dilute $\text{H}_2\text{SO}_4$ and Potassium Permanganate solution and gently warming, decoloration of the Permanganate rapidly occurs, $\text{CO}_2$ being evolved. a) $2\text{KMnO}_4\text{Aq} + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4\text{Aq} + 2\text{MnSO}_4\text{Aq} + 3\text{H}_2\text{O} + 5\text{O}$ b) $5\text{O} + 5\text{H}_2\text{C}_2\text{O}_4 = 5\text{H}_2\text{O} + 10\text{CO}_2$	This reaction is not specially characteristic. Tartrates and many other organic compounds behave similarly, and oxidizable inorganic compounds, e. g. $\text{FeSO}_4\text{Aq}$ , rapidly decolorize Permanganate.

Special Tests for Free Oxalic Acid,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

The body is a white crystalline solid of strongly acid reaction. On thorough ignition no residue is left, but on heating the solid carefully in a test-tube, a crystalline Sublimate of **characteristic branching crystals** can easily be obtained. The free acid by appropriate treatment would also give above tests.

## (16) TARTRATES AND TARTARIC ACID.

Reagent.	Result observed.	Remarks.
1. Heat dry substance	On heating Tartaric Acid and Tartrates char readily, generally giving an odour of burnt sugar.	
2. $\text{H}_2\text{SO}_4$ (concentrated)	On warming Tartaric Acid and Tartrates with conc. $\text{H}_2\text{SO}_4$ , $\text{CO}$ , $\text{CO}_2$ , and $\text{SO}_2$ are evolved.	
3. $\text{CaCl}_2$	Concentrated solutions of Calcium Chloride give with neutral solutions of Tartrates a white precipitate of Calcium Tartrate provided the solution be not too dilute. The precipitate is soluble in cold $\text{KOH}$ or $\text{NaOH}$ , and also in Acetic Acid. e.g. $(\text{NH}_4)_2 \cdot \text{C}_4\text{H}_4\text{O}_6\text{Aq} + \text{CaCl}_2\text{Aq}$ Ammon. Tartrate $= \text{Ca} \cdot \text{C}_4\text{H}_4\text{O}_6 + 2\text{NH}_4\text{ClAq}$ Calcium Tartrate	
4. $\text{KNO}_3$ and ( $\text{CH}_3 \cdot \text{COONa}$ )	Concentrated solutions of Potassium Salts (e.g. $\text{KNO}_3\text{Aq}$ ) when added to Tartaric Acid or a Tartrate give a crystalline precipitate of Potassium Hydrogen Tartrate. The formation of mineral acid must be avoided by adding Sodium Acetate. e.g. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6\text{Aq} + \text{KNO}_3\text{Aq} + \text{CH}_3\text{COONaAq}$ Tartaric Acid $= \text{KH} \cdot \text{C}_4\text{H}_4\text{O}_6 + \text{NaNO}_3\text{Aq} + \text{CH}_3\text{COOHAq}$	
5. $\text{AgNO}_3$	With neutral solutions a white precipitate of Silver Tartrate, $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$ , soluble in $\text{HNO}_3\text{Aq}$ and in $\text{NH}_4\text{OHAq}$ , forms. e.g. $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6\text{Aq} + 2\text{AgNO}_3\text{Aq}$ $= \text{Ag}_2\text{C}_4\text{H}_4\text{O}_6 + 2\text{NaNO}_3\text{Aq}$  A silver mirror can be obtained by appropriate treatment:—Add very dilute $\text{NH}_4\text{OHAq}$ (a few drops of conc. soln. added to test-tube half filled with water) to $\text{AgNO}_3\text{Aq}$ until precipitate first formed nearly dissolves, then add a neutral Tartrate and warm gently (e.g. in beaker of boiling water). The Ammoniacal Silver solution will be reduced and appear as a mirror on the sides of the tube if it is quite clean, otherwise a nearly black precipitate forms. To clean the tube wash first with $\text{NaOHAq}$ and then with water.	

## Special Note regarding Free Tartaric Acid.

The free acid is a white crystalline solid of strongly acid reaction. It would give above reactions on suitable neutralization, &c., and would leave no residue if ignited strongly for some time in a small open crucible.

## DETECTION OF ACIDS.

The acid radicles cannot be tested for so systematically as the metals, but (as already mentioned) it is advisable to have a scheme to fall back upon. Many could be devised, but the following will probably be found most convenient for any given case, taking into consideration the limited number of acids (16) to be looked for. The substance should as a rule be analysed for metals before going on to the acids, and any metals found should be kept in view while testing for acids, in case of interference of the metals present with the tests to be employed; e. g. if silver has been found, one obviously cannot add HCl and BaCl<sub>2</sub>Aq to test for a sulphate, because the silver would at once cause precipitation of silver chloride. There would, however, be no objection to the use of HNO<sub>3</sub>Aq and Ba(NO<sub>3</sub>)<sub>2</sub>Aq in testing for sulphate.

## ANALYTICAL SCHEME FOR ACIDS.

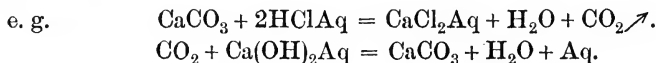
In this scheme the acids are divided into Classes depending upon the conditions under which they can be detected. They are termed Classes rather than Groups because there is not a proper series of Group Reagents.

**CLASS I.** Acids readily detected on adding HClAq or H<sub>2</sub>SO<sub>4</sub>Aq to solid or solution and warming.

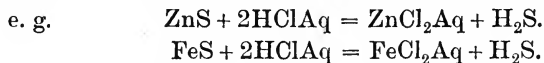
A member of this group would often be detected on dissolving a substance to test for metals.

- (1) H<sub>2</sub>CO<sub>3</sub>.      (2) H<sub>2</sub>S.      (3) HCN.      (4) CH<sub>3</sub>COOH.  
 [(5) H<sub>2</sub>SO<sub>3</sub>.]      [(6) HNO<sub>2</sub>.]

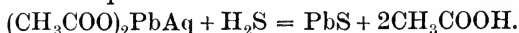
(1) Carbonates evolve CO<sub>2</sub>, detected by effervescence and by the precipitation of calcium carbonate, CaCO<sub>3</sub>, on passing into lime-water.



(2) Sulphides generally give off SH<sub>2</sub>, recognized by its odour and action on paper moistened with (CH<sub>3</sub>COO)<sub>2</sub>Pb.



Ferrous  
Sulphide.

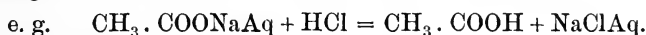


**Note.**—There are a few sulphides which do not evolve  $\text{SH}_2$  under given conditions, e. g. Iron Pyrites ( $\text{FeS}_2$ ), Mercuric Sulphide ( $\text{HgS}$ ), Arsenic Sulphide ( $\text{As}_2\text{S}_3$ ), &c. (See p. 191.)

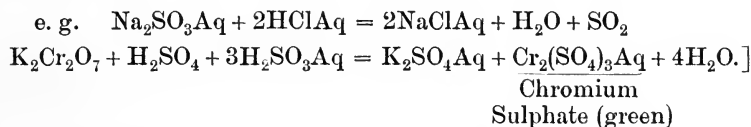
(3) Cyanides are decomposed with evolution of Hydrocyanic Acid,  $\text{HCN}$ , recognized by its odour of bitter almonds.



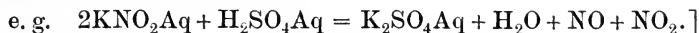
(4) Acetates evolve Acetic Acid, recognized by odour of vinegar.



[(5) Sulphites evolve Sulphur Dioxide,  $\text{SO}_2$ , detected by its pungent characteristic odour of burning sulphur and reducing effect on a solution of potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , which turns green.



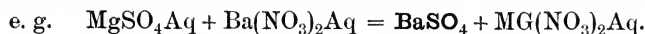
[(6) Nitrites give brown fumes of oxides of nitrogen, recognized by odour and colour.



**CLASS II.** Acids readily detected in strongly acid solution by addition of  $\text{Ba}(\text{NO}_3)_2\text{Aq}$  or  $\text{AgNO}_3\text{Aq}$ .



(7) On addition of  $\text{HNO}_3\text{Aq}$  and  $\text{Ba}(\text{NO}_3)_2\text{Aq}$ , Sulphuric Acid and Sulphates give a white precipitate of barium sulphate,  $\text{BaSO}_4$ .



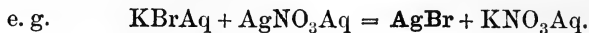
(8) On addition of  $\text{HNO}_3\text{Aq}$  and  $\text{AgNO}_3\text{Aq}$  to a chloride a white precipitate of silver chloride,  $\text{AgCl}$ , soluble in  $\text{NH}_4\text{OHAq}$ , comes down.

**NOTES.**—(a)  $\text{HCN}$  and cyanides would give an exactly similar precipitate of  $\text{AgCN}$ , but should have been detected in the preceding class, unless the candidate for any reason is unable to smell  $\text{HCN}$ .

(b) Concentrated solutions of Oxalates might give a white precipitate of silver oxalate, but the precipitate dissolves on addition of more  $\text{HNO}_3$  and warming.

(9) With Hydrobromic Acid and Bromides  $\text{HNO}_3\text{Aq}$  and  $\text{AgNO}_3\text{Aq}$  give a faintly yellow precipitate of silver bromide,

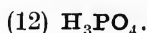
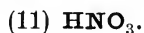
AgBr, soluble with difficulty in  $\text{NH}_4\text{OHAq}$ . (In gaslight the precipitate appears white.)



(10) With hydriodic acid and iodides  $\text{HNO}_3\text{Aq}$  and  $\text{AgNO}_3\text{Aq}$  give a light yellow precipitate of silver iodide, AgI, insoluble in  $\text{NH}_4\text{OHAq}$ .

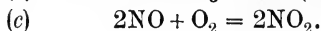
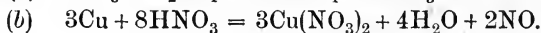


**CLASS III.** Acids which must be tested for by special tests in strongly acid solution.



(11) Test for Nitric Acid by the copper test.

Add to solid or concentrated solution about an equal bulk of concentrated  $\text{H}_2\text{SO}_4$ , and a few pieces of copper turnings. Oxides of nitrogen are evolved and recognized by odour and colour, the solution turning blue, because a solution of copper nitrate is formed.



from air  
in tube.

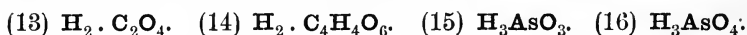
(12) Test for Phosphoric Acid,  $\text{H}_3\text{PO}_4$ , by the Ammonium Nitromolybdate test.

Add to about 2 c.c. of solution of substance 4-10 c.c. of ammonium nitromolybdate and warm to about  $60^\circ\text{C}$ .—i. e. until the heated portion of the test-tube feels uncomfortably hot. A canary yellow precipitate of ammonium phosphomolybdate ( $11\text{MoO}_3 \cdot (\text{NH}_4)_3\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) indicates phosphate.

NOTES.—(a) On boiling arsenates may give a yellow precipitate.

(b) If the substance is insoluble in water, use  $\text{HNO}_3$  and not  $\text{HCl}$  to make the solution for this test.

**CLASS IV.** Acids tested for in approximately neutral solution by reaction with (a)  $\text{CaCl}_2\text{Aq}$ , (b)  $\text{AgNO}_3\text{Aq}$ , [(c)  $\text{FeCl}_3$ ].



Directions for Preparation of a Neutral Solution.

(a) When substance is soluble in water.

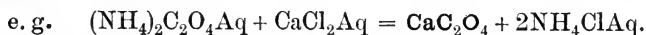
(b) When substance is insoluble in water.



(a) If the substance is soluble in water, and the reaction is markedly acid or alkaline, neutralize a portion in a basin, using  $\text{HNO}_3\text{Aq}$  to bring to neutrality if the solution is alkaline, and dilute ammonia solution if the reaction is acid. Do not attempt to neutralize in a test-tube. Put about 10 c.c. of solution in a porcelain dish, add one drop of litmus, and make neutral by adding acid or alkali as may be necessary, with constant stirring.

(b) If the substance is insoluble in water, but soluble in  $\text{HNO}_3\text{Aq}$  (or  $\text{HClAq}$ ), proceed as follows: Take a small quantity of substance, dissolve in minimum quantity of  $\text{HNO}_3$  in porcelain dish, then add excess of sodium carbonate (solid or solution) and boil for 5 to 10 minutes: filter. The metals will have been completely precipitated as carbonates, and the acids will be in solution as sodium salts. Make neutral by adding  $\text{HNO}_3\text{Aq}$  slowly to boiling solution in porcelain dish, using a drop of litmus as indicator. It is necessary that the solution be boiled during this process of neutralization so as to expel carbon dioxide ( $\text{CO}_2$ ).

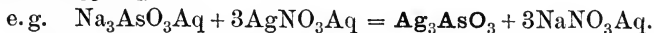
(13) If calcium chloride be added to a neutral solution of an oxalate a white precipitate of calcium oxalate,  $\text{CaC}_2\text{O}_4$ , comes down.



(14) On adding calcium chloride to a neutral solution of a tartrate, a white precipitate of calcium tartrate is formed.

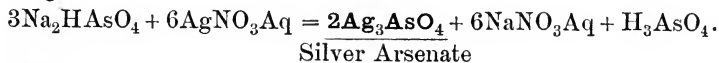


(15) On adding silver nitrate to a neutral solution a yellow precipitate might be silver arsenite,  $\text{Ag}_3\text{AsO}_3$  (or silver phosphate,  $\text{Ag}_3\text{PO}_4$ ).



(16) A chocolate brown precipitate might indicate an arsenate, the brown precipitate being silver arsenate.

e. g.



NOTES:—

(a) A white precipitate formed on addition of silver nitrate to a neutral solution might be silver cyanide ( $\text{AgCN}$ ), silver sulphite ( $\text{Ag}_2\text{SO}_3$ ), silver nitrite ( $\text{AgNO}_2$ ), silver chloride ( $\text{AgCl}$ ), silver oxalate ( $\text{Ag}_2\text{C}_2\text{O}_4$ ), silver tartrate ( $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$ ).

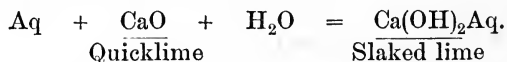
[(b) On addition of ferric chloride to a neutral solution a reddish coloration indicates acetate. It is sometimes advisable to carry out this test at this stage, especially if for any reason one finds it difficult to detect acetic acid by its odour.]

## B. IDENTIFICATION OF METALLIC OXIDES AND HYDROXIDES.

### I. Metallic Oxides.

The Oxides of the Metals might be divided into two classes with regard to their behaviour towards water.

(1) The oxides of Na, K, Ca, Sr, and Ba react with water to give hydroxides which are soluble; e. g.



These hydroxides are strongly alkaline in reaction, and give the tests for soluble hydroxides mentioned below.

(2) The other oxides either react very slightly with water to give soluble hydroxides (e. g. MgO), or are practically insoluble. Most of them, however, dissolve readily in acids and many have characteristic appearance and properties; e. g. HgO is red or yellow; CuO is black; Bi<sub>2</sub>O<sub>3</sub> is yellowish and turns brown on heating; ZnO turns yellow on heating; MgO glows on heating strongly; PbO is light brown or yellow; Fe<sub>2</sub>O<sub>3</sub> is brown; SnO<sub>2</sub> and Sb<sub>2</sub>O<sub>5</sub> are white and very insoluble. Many of these oxides take up carbon dioxide from the air, so that on solution in an acid slight effervescence frequently occurs.

There are no simple direct tests for Oxides, and the analyst must therefore arrive at a conclusion from the appearance, general properties, and behaviour. A couple of examples might make the method of reasoning clear.

#### I. Analysis of Litharge, PbO.

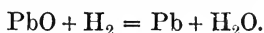
Suppose a light brown substance is being analysed which is insoluble in water, but soluble with difficulty in boiling HCl, and easily soluble in HNO<sub>3</sub>. All the tests for lead are obtained, e. g. reduction on charcoal, precipitation of PbCl<sub>2</sub> on adding HCl to solution in nitric acid, yellow pp. of PbCrO<sub>4</sub> with K<sub>2</sub>CrO<sub>4</sub>Aq, and deep yellow precipitate of PbI<sub>2</sub> with KIAq. The substance is therefore a compound of lead.

Any one with a slight acquaintance with Chemistry should know that nitrate, chloride, bromide, carbonate, phosphate, and sulphate of lead are white solids, the first of which is easily soluble in water, the second and third moderately soluble in hot water, while the others are insoluble, but dissolve in HNO<sub>3</sub>.

The only common yellow and brown compounds of lead are

the monoxide ( $\text{PbO}$ ), the iodide ( $\text{PbI}_3$ ), (and the chromate,  $\text{PbCrO}_4$ ). The chromate dissolves in acid to give a yellow solution; the iodide dissolves in boiling water and can be recrystallized in golden spangles. Iodine could readily be detected in the latter compound by means of  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ , and chromium in the former. Litharge would give no tests for iodide or chromate. By a process of exclusion one would therefore be driven to the conclusion that the substance from appearance, general properties, and behaviour must be an oxide of lead—presumably litharge.

NOTE.—The composition of the substance could easily be quantitatively proved by passing dry hydrogen over a weighed quantity of the heated oxide and weighing the water produced after absorption in tubes containing calcium chloride; e. g.



Such an investigation lies outside elementary analysis.

## II. Analysis of $\text{ZnO}$ .

Zinc oxide is a white solid, which turns yellow on heating and white again on cooling. It is insoluble in water, but easily dissolves in dilute  $\text{HCl}$ ,  $\text{HNO}_3$ , or  $\text{H}_2\text{SO}_4$ . The tests for zinc would readily be obtained, and the analyst should then reason as follows:—

(1) As the body is insoluble in water it cannot be zinc chloride, bromide, iodide, nitrate, or sulphate, which are easily soluble.

(2) From solubility it might be oxide, hydroxide, carbonate, sulphide, or phosphate. It might also possibly be oxalate.

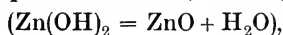
(3) The substance could not be carbonate or sulphide, because neither  $\text{CO}_2$  nor  $\text{H}_2\text{S}$  is evolved on solution in  $\text{HCl}$ .

(4) On dissolving in  $\text{HNO}_3$  and testing with ammonium nitromolybdate no coloration or precipitate is obtained; therefore it is not a phosphate.

(5) By exclusion the subject must therefore be oxide or hydroxide.

[NOTE.—Zinc oxalate would give zinc carbonate on heating with slight charring and would give a mixture of  $\text{CO}$  and  $\text{CO}_2$  with conc.  $\text{H}_2\text{SO}_4$ .]

The student would not as a rule be expected to discriminate between oxide and hydroxide, but one might point out that the hydroxide on cautious heating in a long dry tube would give off a considerable proportion of water, forming the oxide



while the oxide would give off no water and would turn yellow on heating.

From above examples one might therefore conclude that a decision as to whether a body is an **Oxide** or **Hydroxide** depends upon the application of general chemical knowledge in an intelligent manner. The **Tables of Common Compounds of the respective Metals** given opposite the **Lists of Tests** should be of great help to a beginner in getting a general idea as to the relationships of the compounds of the metals. When a student requires more complete information he should consult a theoretical handbook.

## II. Hydroxides of the Metals.

The hydroxides might, like the oxides, be divided into two classes with regard to their behaviour towards water.

(1) The hydroxides soluble in water:  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ .

(2) The other hydroxides are either insoluble or very slightly soluble. A few of these insoluble hydroxides are of characteristic appearance, e.g. copper hydroxide,  $\text{Cu}(\text{OH})_2$ , is blue, and ferric hydroxide,  $\text{Fe}(\text{OH})_3$ , brown.

### Reactions of Soluble Hydroxides.

Reagent.	Observation.
1) <b>Litmus</b>	<b>Strongly alkaline</b> in reaction. The caustic alkalies have a soapy feel, and Ammonium Hydroxide a characteristic odour, owing to loss of $\text{NH}_3$ .
2) <b><math>\text{NH}_4\text{ClAq}</math> and boil</b>	On boiling an Ammonium Salt with a soluble Hydroxide, Ammonia is evolved. e.g. $\text{NH}_4\text{ClAq} + \text{NaOHAq} = \text{NaClAq} + \text{H}_2\text{O} + \text{NH}_3 \uparrow$ $2\text{NH}_4\text{ClAq} + \text{Ca}(\text{OH})_2\text{Aq} = \text{CaCl}_2\text{Aq} + 2\text{H}_2\text{O} + 2\text{NH}_3 \uparrow$
3) <b><math>\text{AgNO}_3\text{Aq}</math></b>	A <b>greyish precipitate</b> , consisting chiefly of <b>Silver Oxide</b> , $\text{Ag}_2\text{O}$ , is obtained. (Note.—In the case of $\text{NH}_4\text{OH}$ the precipitate is so easily soluble in excess of reagent, that without special precautions it would hardly be seen.) e.g. $2\text{AgNO}_3\text{Aq} + 2\text{NaOHAq} = \text{Ag}_2\text{O} + \text{H}_2\text{O} + 2\text{NaNO}_3\text{Aq}$ $2\text{AgNO}_3\text{Aq} + \text{Ca}(\text{OH})_2\text{Aq} = \text{Ag}_2\text{O} + \text{H}_2\text{O} + \text{Ca}(\text{NO}_3)_2\text{Aq}$
4) <b><math>\text{CuSO}_4\text{Aq}</math></b>	<b>Blue precipitate</b> of Copper Hydroxide, $\text{Cu}(\text{OH})_2$ . $\text{CuSO}_4\text{Aq} + 2\text{NaOHAq} = \text{Cu}(\text{OH})_2 + \text{Na}_2\text{SO}_4\text{Aq}$
5) <b><math>\text{FeCl}_3\text{Aq}</math></b>	<b>Brown precipitate</b> of Ferric Hydroxide. $\text{FeCl}_3\text{Aq} + 3\text{NaOHAq} = \text{Fe}(\text{OH})_3 + 3\text{NaClAq}$

**COMPLETE SUMMARY OF METHOD OF PROCEDURE  
IN CARRYING OUT TESTS FOR ACID RADICLES  
AND FOR SOLUBLE METALLIC HYDROXIDES.**

**I. Dry Tests.**

**II. Wet Tests.**

The wet tests should be carried out in the given order, but the dry tests need not be made before the wet tests. It will be found advisable, however, to carry out the first of the dry tests—viz. heating a substance in a small tube—before going on to test for Class IV of the acids, as the charring of tartrates would save trouble.

**I. DRY TESTS.**

Experiment.	Result.
1. Heat a small quantity of solid in a narrow tube of hard glass.	<p>a) Extensive charring indicates Tartaric Acid or Tartrate.</p> <p>b) Acetates and Oxalates may char slightly.</p> <p>c) Brown fumes of characteristic odour would indicate Nitrates (or Nitrites).</p> <p>d) Ammonium, Mercury, Tin, Arsenic, or Antimony Compounds might volatilize.</p> <p>e) Sulphur might come off from Persulphides, e. g. <math>\text{FeS}_2 = \text{FeS} + \text{S}</math>.</p>
2. Heat small quantity of substance with concentrated $\text{H}_2\text{SO}_4$ in test-tube.	<p>a) Extensive charring indicates Tartrates or Tartaric Acid.</p> <p>b) Acetates and Oxalates might char slightly.</p> <p>c) <math>\text{CO}</math> evolved, which would burn with blue flame, might indicate Oxalate, Oxalic Acid, or Cyanide.</p> <p>d) Fuming colourless gas—pungent odour—<math>\text{HCl}</math>.</p> <p>e) Fuming colourless or brown gas—Nitric Peroxide odour—<math>\text{HNO}_3</math> or <math>\text{HNO}_2</math>.</p> <p>f) Fuming brown gas—odour of Bromine—indicates mixture of <math>\text{Br}_2</math> and <math>\text{HBr}</math> from Bromide.</p> <p>g) Fuming gas and violet vapour indicates <math>\text{HI}</math> and <math>\text{I}_2</math> from Iodide.</p> <p>h) <math>\text{CO}_2</math> evolved with effervescence indicates Carbonate.</p> <p>i) <math>\text{SH}_2</math> evolved indicates Sulphide.</p> <p>j) Odour of vinegar indicates Acetate.</p> <p>k) <math>\text{HCN}</math> evolved indicates Cyanide.</p> <p>l) <math>\text{SO}_2</math> evolved indicates Sulphite.</p>

## II. WET TESTS FOR ACID RADICLES AND SOLUBLE METALLIC HYDROXIDES.

**Preliminary.** If solution has been prepared by boiling with water, test reaction towards litmus:—

(1) Strongly acid reaction may indicate (a) free acid, (b) acid salt, or (c) salts with acid reaction [e. g.  $\text{CuSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$ ].

(2) Neutral reaction may indicate a neutral salt.

(3) Alkaline reaction may indicate (a) Soluble Metallic Hydroxide, e. g.  $\text{NaOH} \cdot \text{Ba}(\text{OH}_2)$ , (b) salt with alkaline reaction, e. g.  $\text{KCN} \cdot \text{Na}_2\text{CO}_3$ .

Experiment.	Result observed.	Acid or Salt indicated.	Confirmatory Tests. (Consult Lists of Reactions under respective acids.)
1. Add to conc. solution or solid $\text{HCl}$ or $\text{H}_2\text{SO}_4$ and warm gently.	<p>a) <math>\text{CO}_2</math> evolved as indicated by passage into lime-water.</p> <p>b) <math>\text{SH}_2</math> evolved as indicated by odour and reaction with <math>(\text{CH}_3 \cdot \text{COO})_2\text{Pb}</math>.</p> <p>c) <math>\text{HCN}</math> evolved as indicated by odour of bitter almonds.</p> <p>d) Acetic Acid evolved—odour of vinegar.</p> <p>[e] <math>\text{SO}_2</math> evolved—odour of burning sulphur.</p> <p>[f] Brown fumes.</p>	<p>a) Carbonate</p> <p>b) Sulphide</p> <p>c) Cyanide</p> <p>d) Acetate</p> <p>e) Sulphite]</p> <p>f) Nitrite]</p>	<p>If Carbonate is soluble in water one can confirm by addition of</p> <p>1) <math>\text{AgNO}_3</math> 2) <math>\text{CaCl}_2</math>, &amp;c.</p> <p>If sulphide is soluble in water one could confirm by 1) <math>\text{AgNO}_3\text{Aq}</math> 2) <math>\text{CuSO}_4\text{Aq}</math> Prussian blue test.</p> <p>1) <math>\text{FeCl}_3\text{Aq}</math> to neutral solution. 2) Ethyl Acetate test.</p> <p>1) Paper moistened with <math>\text{K}_2\text{Cr}_2\text{O}_7\text{Aq}</math>.</p> <p>1) Acetic Acid and <math>\text{FeSO}_4</math>. 2) <math>\text{H}_2\text{SO}_4</math>, <math>\text{KI}</math>, and starch.</p>
2. To original solution add $\text{HNO}_3$ and $\text{Ba}(\text{NO}_3)_2$ (or if Group I of Metals be absent, $\text{HCl}$ and $\text{BaCl}_2$ can be used).	White precipitate may be $\text{BaSO}_4$ .	Sulphate or Sulphuric Acid	<p>1) <math>(\text{CH}_3 \cdot \text{COO})_2\text{PbAq}</math>. 2) <math>\text{Na}_2\text{CO}_3</math> to solid and heat on Carbon. <math>\text{Na}_2\text{S}</math> is formed. Place on moist silver coin.</p>
3. To original solution add $\text{HNO}_3\text{Aq}$ and $\text{AgNO}_3\text{Aq}$ .	<p>a) White precipitate may be <math>\text{AgCl}</math> (or <math>\text{AgCN}</math>). The pp. is soluble in <math>\text{NH}_4\text{OHAq}</math>.</p> <p>b) Faintly yellow precipitate may be <math>\text{AgBr}</math> (soluble in <math>\text{NH}_4\text{OH}</math> with difficulty).</p> <p>c) Light yellow precipitate insoluble in <math>\text{NH}_4\text{OH}</math> may be <math>\text{AgI}</math>.</p>	<p>Chloride or Hydrochloric Acid</p> <p>Bromide</p> <p>Iodide</p>	<p>1) <math>\text{MnO}_2</math> and <math>\text{H}_2\text{SO}_4</math>—bleaching action and odour. 2) <math>\text{H}_2\text{SO}_4</math> to solid.</p> <p>1) <math>\text{Cl}_2\text{Aq}</math> and <math>\text{CS}_2</math> or <math>\text{CHCl}_3</math>. Bromine set free. 2) <math>\text{MnO}_2</math> and <math>\text{H}_2\text{SO}_4</math>. Bromine liberated.</p> <p>1) <math>\text{Cl}_2\text{Aq}</math> and <math>\text{CS}_2</math> or <math>\text{CHCl}_3</math>. <math>\text{I}_2</math> set free. 2) <math>\text{MnO}_2</math> and <math>\text{H}_2\text{SO}_4</math>. Iodine liberated.</p>

# WET TESTS FOR ACID RADICLES AND SOLUBLE METALLIC HYDROXIDES (continued).

Experiment.	Result observed.	Acid or Salt indicated.	Confirmatory Tests. (Consult Lists of Reactions under respective acids.)
4. Test for $\text{HNO}_3$ by adding conc. $\text{H}_2\text{SO}_4$ and Cu to solid or concentrated solution.	Brown fumes.	Nitrate or Nitric Acid	Brown ring test.
5. Test for $\text{H}_3\text{PO}_4$ by adding Ammon. Nitromolybdate and warming gently.	Canary yellow precipitate.	Phosphates or Phosphoric Acid	1) $\text{AgNO}_3$ to neutral solution. Yellow pp. of $\text{Ag}_3\text{PO}_4$ . 2) $\text{NH}_4\text{ClAq}$ , $\text{NH}_4\text{OHAq}$ , and $\text{MgSO}_4\text{Aq}$ . White precipitate of $\text{Mg} \cdot \text{NH}_4\text{PO}_4$ . Magnesium Ammon. Phosphate.
6. To neutral solution (which may be original solution) add Calcium Chloride, $\text{CaCl}_2\text{Aq}$ .	White precipitate may be $\text{CaC}_2\text{O}_4$ or $\text{Ca} \cdot \text{C}_4\text{H}_4\text{O}_6$ .	a) Oxalate or b) Tartrate	a) Confirm 1) $\text{H}_2\text{SO}_4$ to solid. 2) $\text{AgNO}_3\text{Aq}$ to neutral solution. b) Confirm Dry Test—charring.
7. To neutral solution (which may be original solution) add Silver Nitrate, $\text{AgNO}_3\text{Aq}$ .	a) Yellow precipitate may be $\text{Ag}_3\text{AsO}_3$ , b) or $\text{Ag}_3\text{FO}_4$ , c) Chocolate brown precipitate may be $\text{Ag}_3\text{AsO}_4$ .	a) Arsenite or [b] Phosphate c) Arsenate	a) 1) $\text{H}_2\text{S}$ and $\text{HCl}$ gives yellow precipitate. 2) Reinsch's test. b) See above. c) Reduce by boiling with Sulphurous Acid solution and then try 1) $\text{H}_2\text{S}$ and $\text{HCl}$ . 2) Reinsch's test.
	d) White precipitate may be $\text{AgCN}$ , $\text{Ag}_2\text{SO}_3$ , $\text{AgNO}_2$ , $\text{AgCl}$ , $\text{Ag}_2\text{C}_2\text{O}_4$ , or $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$ .	Cyanide Sulphite Nitrite Chloride Oxalate Tartrate	Already indicated.
8. If detection of odour in Test 1 has been difficult add $\text{FeCl}_3\text{Aq}$ to neutral solution.	Brownish red coloration with brown precipitate on boiling for some time.	Acetate	See Test 1, above.

## Test for Soluble Hydroxides.

9. If reaction be alkaline add $\text{AgNO}_3\text{Aq}$ to original solution.	Greyish brown precipitate of Silver Oxide.	Soluble Hydroxide	1) Alkaline reaction. 2) $\text{CuSO}_4\text{Aq}$ . 3) $\text{NH}_4\text{ClAq}$ and boil. $\text{NH}_3$ is evolved. See p. 212.
-------------------------------------------------------------------------------	--------------------------------------------	-------------------	------------------------------------------------------------------------------------------------------------------------------------------

### Methods of recording Results of Analysis.

Records of analyses need not be written out very fully provided that they are presented in a logical manner. Equations should be given for positive reactions. A specimen analysis of a simple salt, showing how a beginner should record his results, may be found useful.

### Specimen Analysis.

**Appearance.** White crystalline solid.

**Solubility.** Easily soluble in water. Solution is neutral, therefore subs. is probably a neutral salt.

**Preliminary Test.** Heated a few crystals strongly in a tube of hard glass. Brown fumes of  $\text{NO}_2$  evolved, presumably indicating a nitrate.

### A. Analysis for Metal.

Experiment.	Observation.	Inference.
1) To solution added $\text{HClAq.}$	No pp.	Absence of Group I—Ag, $\text{Hg}^{\text{ous}}$ , Pb.
2) To same solution added $\text{H}_2\text{S.}$	No pp.	Absence of Group II—(Pb), Cu, $\text{Hg}^{\text{lc}}$ , Bi, As, Sb, Sn.
3) To original solution added $\text{NH}_4\text{ClAq}$ and $\text{NH}_4\text{OHAq.}$	No pp.	Absence of Group III— $\text{Fe}^{\text{ous}}$ , $\text{Fe}^{\text{lc}}$ , Al, Cr.
4) To same solution added $(\text{NH}_4)_2\text{S.}$	No pp.	Absence of Group IV—Zn, Mn.
5) To same solution added $(\text{NH}_4)_2\text{CO}_3\text{Aq.}$	White pp.	Ba, Sr, or Ca present.

Filtered and tested precipitates by heating on platinum wire moistened with conc.  $\text{HCl}$ . Green flame. Barium is present.

### Confirmatory Tests:—

(a) Dissolved the pp. in acetic acid and added  $\text{K}_2\text{CrO}_4\text{Aq.}$  Characteristic yellow pp. of  $\text{BaCrO}_4$ .

(b) To original solution added  $\text{CaSO}_4\text{Aq.}$  White pp. Barium Sulphate.



**B. Analysis for Acid.**

Confirmed  $\text{HNO}_3$ , as indicated in the preliminary test, by adding to a conc. sol. conc.  $\text{H}_2\text{SO}_4$  and Cu turnings and warming gently.  $\text{NO}_2$  evolved—solution turns blue.

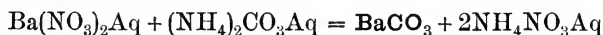
(NOTE.—The brown ring test may also be used, but is quite unnecessary under the circumstances.)

**Conclusion.** The substance is Barium Nitrate.

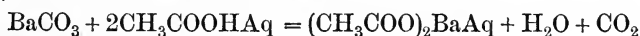
Equations for positive reactions carried out :—

(a) **For Metal.**

(1) Precipitation as carbonate.



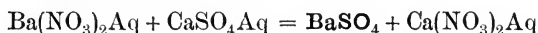
(2) Solution of carbonate in acetic acid.



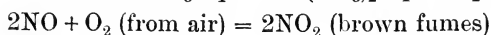
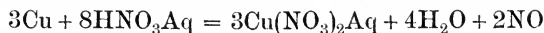
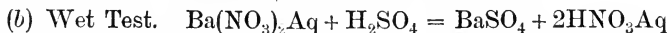
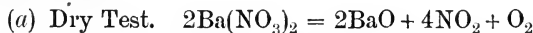
(3) Precipitation as chromate.



(4) Precipitation as sulphate.



(b) **For Acid.**



## MEMORANDA

## **MEMORANDA**

## MEMORANDA

## PART V

### QUANTITATIVE ANALYSIS



## PART V

### QUANTITATIVE ANALYSIS

IN the chemical investigation of a body qualitative analysis, where one merely determines what elements or groups of elements are present, plays a preliminary part. If the substance seems to be a compound or mixture of compounds and we wished to ascertain the exact composition, we would next proceed to make a **quantitative analysis**, in which we determine the actual weights of the elements or groups of elements present in a given weight of substance. So far we have considered only qualitative analysis, and we now naturally come to **quantitative estimations**.

**Quantitative Analysis** might be divided into two different types of determinations:

#### A. Gravimetric Analysis.

#### B. Volumetric Analysis.

In **Gravimetric Analysis** we determine the percentages of elements and groups of elements (e. g.  $\text{SO}_4$ ) in a substance by processes involving weighing the products of reactions.

In **Volumetric Analysis** we estimate the percentages of substances in solution by finding the volumes of reagents of known strength required to complete definite reactions.

#### A. Gravimetric Analysis.

The principles of gravimetric analysis are generally more readily grasped than those of volumetric analysis, so that a few typical determinations of the former type will first be considered.

##### I. Determination of the percentage of Oxygen in Potassium Chlorate.

**Method.**—Weigh into a small crucible 0.5 to 1.0 gram of potassium chlorate and heat on pipeclay triangle over a Bunsen flame for 15–20 minutes, as indicated in Fig. 14. Oxygen will be driven off. Equation:  $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ . Weigh. Heat again for 5–10 minutes and weigh again. If the weight is the

same as before, calculate the percentage of oxygen present. If not, reheat and reweigh until weight is constant. The cooling before weighing should be carried out in a desiccator. A desiccator is a stout glass vessel, containing some hygroscopic material such as calcium chloride or conc. sulphuric acid, and bodies which have been heated should invariably be allowed to cool

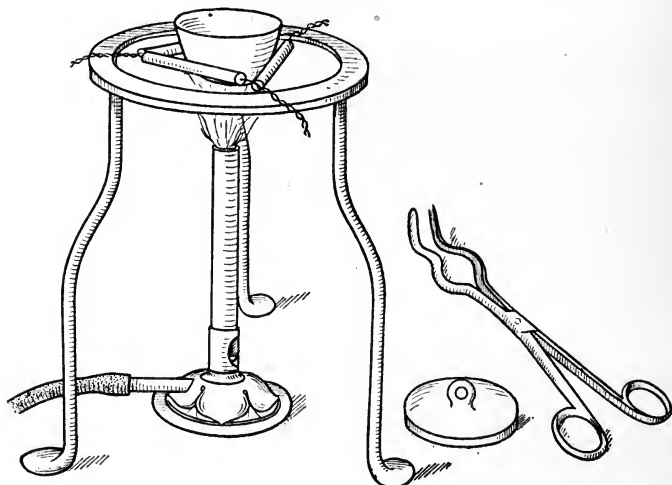


FIG. 14. METHOD OF HEATING A CRUCIBLE ON PIPECLAY TRIANGLE.

in a desiccator before weighing, as this gets over difficulties in connexion with condensation of moisture from the atmosphere. Enter the results as follows:—

	Grams.
Weight of crucible + potassium chlorate	= 17.320
Weight of empty crucible	= 16.320
Weight of potassium chlorate taken	= 1.00 Gram.

After heating 20 min. weight of crucible + residue = 16.928

Heated for 5 min. and reweighed, wt. = 16.928

The weight of oxygen in 1 gram of potassium chlorate is therefore  $17.32 - 16.928 = 0.392$  gram.

The chlorine in the residue can be easily estimated by a volumetric determination, by dissolving in water, making up to a known volume, say 100 c.c., taking a fractional part of this and titrating against standard silver nitrate, using potassium chromate as indicator as described on p. 249.



The quantity of **oxygen** and **chlorine** in a certain weight of chlorate having been determined, the **potassium** can be calculated by **difference**, and from the results a formula could be found.

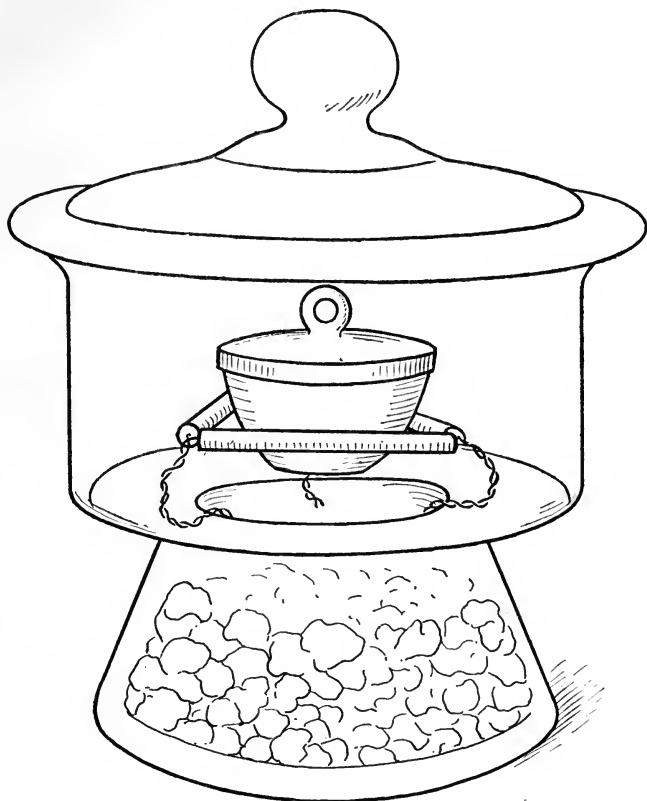


FIG. 15. DESICCATOR CONTAINING CALCIUM CHLORIDE AS DRYING AGENT.

	Gram.
e. g. Wt. of oxygen in 1 gram of $\text{KClO}_3$	= 0.392
Wt. of chlorine in 1    "    "    "	= 0.290
Wt. of potassium by difference	= 0.318
	<hr/> 1.000

From above values one could determine the formula of the body (supposing it to be unknown) in the following way:—

(1) Find percentage of **Oxygen**, **Chlorine**, and **Potassium** present.

The percentages or weights in 100 grams (or parts by weight) could easily be found by multiplying by 100.

Percentage of oxygen	$0.392 \times 100 = 39.2$
„ „ chlorine	$0.29 \times 100 = 29.0$
„ „ potassium	$0.318 \times 100 = 31.8$
	<hr/> 100.0

(2) Find the relative number of atoms of each element present in the molecule.

If the weights of atoms of oxygen, chlorine, and potassium were the same, the percentage values would indicate the relative number of atoms of each element in the molecule. But the atoms of oxygen, chlorine, and potassium have different weights, and to get values which will represent the relative number of atoms of each element in the molecule one must therefore divide percentages by atomic weights.

Oxygen	$\frac{39.2}{16} = 2.45$	$\frac{2.45}{0.82} = 3$
Chlorine	$\frac{29.0}{35.5} = 0.82$	$\frac{0.82}{0.82} = 1$
Potassium	$\frac{31.8}{39} = 0.82$	$\frac{0.82}{0.82} = 1$

Dividing the values obtained by 0.82, the smallest number, so as to get integers, the relative number of atoms of oxygen, chlorine, and potassium are 3, 1, and 1 respectively, indicating that the simplest formula for potassium chlorate as determined by analysis is  $\text{KClO}_3$ . This need not necessarily be the real formula. If the formula were  $\text{K}_2\text{Cl}_2\text{O}_6$  identical results would be obtained for percentage composition. A determination of Molecular Weight would be necessary in order to get the real formula.

## II. Investigation of Crystallized Barium Chloride.

**Qualitative Analysis.** Barium chloride is a white crystalline solid easily soluble in water, and on testing for metals and acids in ordinary way barium and chloride could readily be detected. Water of crystallization would be indicated by heating a small quantity of substance in a dry tube. Water would be deposited on sides of tube, and crystals would fall to pieces.

**Quantitative Analysis.** The qualitative results would indicate that barium, chlorine, and water of crystallization should be determined.

(1) Water of Crystallization.

**Preliminary.** A moderate quantity of the crystals should preferably be dissolved in water, recrystallized, and dried on filter paper at ordinary temperature. They might then be powdered and placed in a small weighing bottle (Fig. 16). Weigh into a porcelain crucible 0.25 to 1 gram of the powder, and heat carefully either in an air oven (Fig. 16) to a temperature of about 200° C. or directly over a small flame. Heat for about thirty

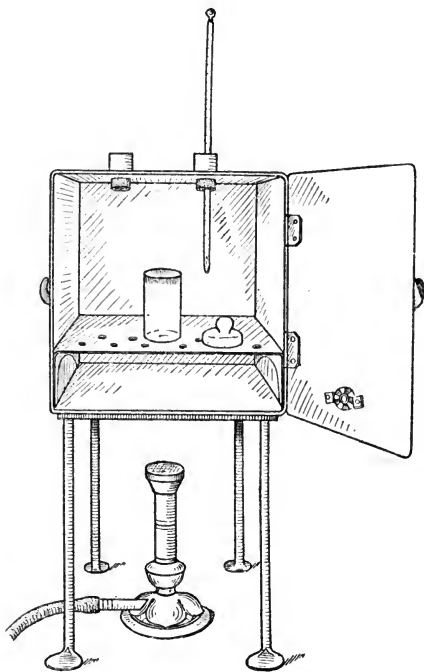


FIG. 16. DRYING OVEN WITH WEIGHING BOTTLE.

minutes, weigh, reheat for ten minutes, and weigh again. Repeat until weight is constant. The cooling should take place in a desiccator.

**NOTES.**—(a) If a compound containing water of crystallization decomposes on heating strongly, the air oven must be employed for similar determinations to that described above; e.g. the water of crystallization of copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) should be determined in an air oven by heating to 210° C.

(b) It will generally be found that 0.3 to 0.5 gram of a substance is quite sufficient for any quantitative estimation, provided the weighing can be made to one milligram. One gram is indicated as taken here merely to simplify calculations.

	Grams.
e. g. Weight of empty crucible	= 16.320
Weight of crucible and barium chloride	= 17.320
Weight of crystallized barium chloride taken	= 1.0 gram
After heating for thirty minutes in air oven weight	= 17.180
Reheated for ten minutes	" = 17.172
Do.	" = 17.172
Weight of crucible + anhydrous barium chloride	= 17.172
Weight of crucible + hydrated barium chloride	= 17.320
Weight of water driven off	= 0.148 gram

## (2) Estimation of Barium by precipitation as Barium Sulphate, $\text{BaSO}_4$ .

Dissolve the anhydrous barium chloride remaining in the crucible in water in a small beaker, add 1–2 c.c. of concentrated HCl so as to render strongly acid, heat to boiling, and add slowly, with stirring, to the boiling solution hot dilute sulphuric acid as long as a precipitate forms. Boil for a few minutes, and then allow to settle. Filter off through a close-grained filter paper, the ash of which is known or negligible, and wash the precipitate on the filter with hot water until the wash water passing through gives practically no reaction with  $\text{BaCl}_2\text{Aq}$ , indicating that excess of sulphuric acid has been washed away. Remove the filter paper and its contents from the funnel, close the cone so as to form a quadrant of a circle, and press between filter paper so as to remove large excess of moisture. Make into a roll, starting with the apex of the cone, and then throw into a red-hot platinum or porcelain crucible. Heat strongly over Bunsen flame until a nearly white residue remains, breaking up any lumps with a piece of wire. Weigh, and from the weight of barium sulphate found calculate the weight of barium in barium chloride taken.

Results :—	Grams.
Weight of crucible + barium sulphate ( $\text{BaSO}_4$ )	= 17.275
Weight of empty crucible	= 16.320
Weight of barium sulphate	= 0.955 gram

The molecular weight of barium sulphate is  $137 + 32 + 64 = 233$ , and 137 parts by weight of barium must be present in 233 parts by weight of barium sulphate.

$$\therefore \text{Wt. of barium in } 0.955 \text{ gms. BaSO}_4 = \frac{137}{233} \times 0.955 = 0.5620 \text{ gms.}$$

This must be the weight of barium sulphate in one gram of crystallized barium chloride.

(3) **Chlorine.** The percentage of chlorine can readily be determined volumetrically, using excess of potassium chromate as indicator. (See p. 219.)

#### Determination of Formula from results.

(1) Wt. of water in 1 gram subs. = 0.148 gram = 14.8 per cent.

(2) Wt. of barium in 1 gram „ = 0.562 „ = 56.2 „

(3) Wt. of chlorine in 1 gram „ = 0.290 „ = 29.0 „

The relative number of molecules of water to the barium and chlorine atoms in the molecule is found in the same way, viz. by dividing the percentages by numbers representing atomic weights (or molecular weight for a group like water).

Water	$\frac{14.8}{16 + 2} = 0.82$	$\frac{0.82}{0.41} \equiv 2 \equiv 2\text{H}_2\text{O}$
Barium	$\frac{56.2}{137} = 0.41$	$\frac{0.41}{0.41} \equiv 1 \equiv \text{Ba}$
Chlorine	$\frac{29.0}{35.5} = 0.82$	$\frac{0.82}{0.41} \equiv 2 \equiv \text{Cl}_2$

The simplest formula would therefore be  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .

## B. VOLUMETRIC ANALYSIS.

Volumetric determinations of the weights of elements or radicles present in given weights of bodies can only be effected under certain definite conditions.

(1) The end point of the reaction must be sharply defined. If one is determining quantities by adding a measured volume of a reagent, one must know when the reaction which is being carried out is completed. This is often effected by the addition of an indicator which becomes coloured or alters in colour when the reaction is complete, e. g. litmus, in alkalimetry and acidimetry; but sometimes one of the reacting bodies acts as indicator, e. g. in case of oxidation of substances by potassium permanganate as detailed below.

(2) The change which takes place on adding the reagent must be known, so that an equation can be written expressing the reaction. From the equation one can calculate the relative weights of reagent and reacting body.

In Volumetric Analysis one uses solutions of reagents of known strength, so that one can calculate the weight of reagent in any volume which may be used.

One could employ solutions of any strength one pleased; e. g. one could use reagents containing 100 grams to the litre. If one used 25 c.c. of such a solution for a certain determination then obviously the weight of reagent present is

$$\frac{25}{1000} \times \frac{100}{1} = 2.5 \text{ grams.}$$

From the equation expressing the reaction one could then readily determine the weight of reacting substance which had been acted upon by that weight of reagent.

It is more convenient, however, to deal with what are termed **Normal Solutions**, or solutions bearing a simple relationship to such solutions.

**DEFINITION.**—A **Normal Solution** is defined as one which—

(a) contains one gram of replaceable hydrogen or its equivalent per litre, or

(b) in the case of oxidizing agents (e. g.  $\text{KMnO}_4$ ) contains in one litre such a weight of substance as will oxidize one gram of hydrogen, or give up 8 grams of oxygen to an oxidizable body.

**Normal Solutions** are generally designated by the symbol **N**.

Such solutions, and submultiples, are in common use. **Half** or **semi-normal** solutions are represented as  $\frac{N}{2}$ , **tenth** or **decinormal** solutions as  $\frac{N}{10}$ , and so on. Multiples of Normal, e. g. **2N**, **3N**, are sometimes employed.

It follows from above Definition that the strengths of normal solutions of a few common acids and bases would be as follows:—

(1) **HCl**. A normal solution of HCl would contain the molecular weight in grams, viz. **36.5 grams per litre**, because 36.5 grams contain 1 gram of replaceable hydrogen.

(2) **HNO<sub>3</sub>**. A normal solution of HNO<sub>3</sub> would contain molecular weight in grams, viz. **63 grams per litre**, because 63 grams of HNO<sub>3</sub> contain 1 gram of replaceable hydrogen.

(3) **H<sub>2</sub>SO<sub>4</sub>**. A normal solution of H<sub>2</sub>SO<sub>4</sub> would contain half the molecular weight in grams, viz.  $\frac{98}{2} = 49$  **grams per litre**, because 98 grams of sulphuric acid contain 2 grams of displaceable hydrogen.

(4) **H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O**. A normal solution of oxalic acid would contain half the molecular weight in grams, viz.  $\frac{126}{2} = 63$  **grams per litre**, because 126 grams contain 2 grams of replaceable hydrogen.

In the case of **alkaline solutions** one has to consider how many hydrogen atoms the metal present represents. The hydroxides might be regarded as derived from water by replacement of one of the two hydrogen atoms in each molecule by metal; e. g. **NaOH**. Normal solution of NaOH would contain the molecular weight in grams = **40 grams in one litre**, because 1 atom of sodium is equivalent to 1 atom of hydrogen.

Similarly a **Normal Solution of KOH** contains **56 grams per litre**. In the case of a body like sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>, a normal solution would contain half the molecular weight in grams, viz.  $\frac{106}{2} = 53$  **in one litre**.

#### Apparatus required in Volumetric Determinations.

In volumetric analysis one requires (a) burettes, (b) measuring flasks, (c) pipettes, and (d) graduated cylinders. These are indicated in Figs. 17 and 18.

(a) **Burettes** are narrow graduated tubes usually capable of delivering any quantity up to 50, 25, or 10 c.c., depending upon capacity, and graduated to tenths of a c.c. For ordinary laboratory work a burette graduated to give 50 c.c., closed at the

bottom by a glass tap, is preferable. The two common types are represented in Fig. 17.

(b) **Measuring flasks.**

These are flasks with moderately narrow necks, which contain definite volumes at a certain temperature when filled up to a mark on the neck. The volumes are generally one litre or some simple fraction thereof, e. g. 500, 250, 200, or 100 c.c., and the temperature is generally  $15^{\circ}\text{C}$ ., which as a rule is approximately room temperature, so that temperature corrections are as a rule negligible. See Fig. 18.

(c) **Pipettes** are generally cylindrical glass tubes connected to narrow pieces of tubing at each end as indicated in the figure. The tip of the pipette is drawn out to form a capillary. A mark is

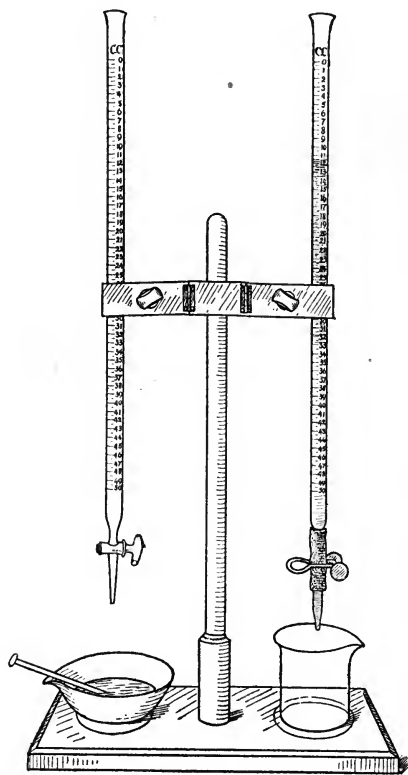


FIG. 17. VOLUMETRIC APPARATUS.  
Burettes with Glass Stopper and  
Pinchclip respectively.

etched on the upper piece of narrow tubing to indicate the height to which a liquid must be taken to enable one to deliver the volume indicated on the pipette. The pipettes most generally used are those for 100, 50, 25, or 10 c.c. capacity respectively. See Fig. 18.



(d) **Graduated cylinders** are merely used for measuring out approximate quantities. Their width is such that any slight error in reading volume may mean a considerable error in calculation. A 100 c.c. measure is indicated in Fig. 18.

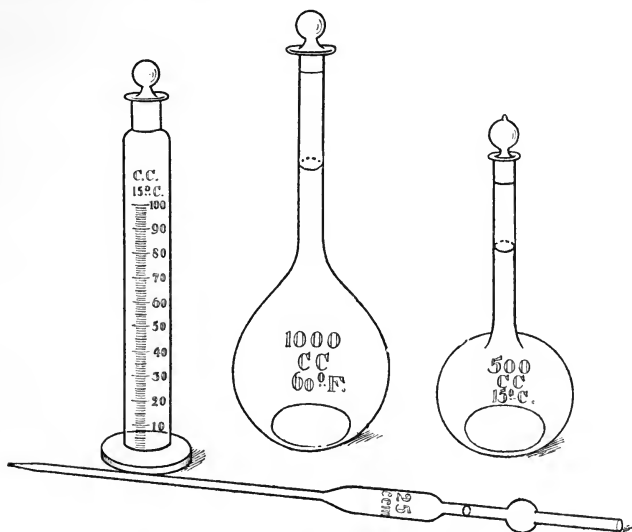


FIG. 18. VOLUMETRIC APPARATUS. Measuring Cylinder, Measuring Flasks, and Pipette.

## ACIDIMETRY AND ALKALIMETRY.

The determination of the quantities of acids and alkalis in solution is termed acidimetry and alkalimetry. Three indicators are in common use for indicating the end point in measurements of this kind, viz. litmus, methyl orange, and phenol phthalein. The action of these indicators depends upon the formation of coloured ions when free acid or alkali is in excess.

Litmus in neutral solution is violet. It turns red with acids and blue in alkaline solution, as already noted.

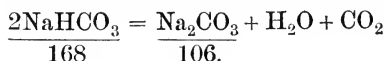
Methyl orange is orange in neutral solution, red in acid solution, and yellow in alkaline solution.

Phenol phthalein is colourless in neutral or acid solutions, but scarlet in alkaline solution.

## Preparation of Standard Solutions.

The preparation of standard solutions is of primary importance in volumetric analysis. As a rule, a student is given standard solutions, but he should clearly understand how they can be prepared.

In acidimetry and alkalimetry, if one solution is prepared of absolutely correct strength, it is easy to prepare others. The initial standard solution chosen is generally one of pure sodium carbonate. As already noted, a standard solution of sodium carbonate would contain  $\frac{106}{2} = 53$  grams per litre. There is no necessity to prepare a litre of solution. For all practical purposes 100 c.c. is enough, and one can proceed as follows: Weigh roughly into a platinum (or porcelain) dish enough pure sodium bicarbonate to give rather more than  $\frac{53}{10}$  grams of sodium carbonate on heating—the quantity required to give a normal solution when dissolved in water and made up to 100 c.c. The equation expressing the decomposition of  $\text{NaHCO}_3$  to give  $\text{Na}_2\text{CO}_3$  would be:—



This equation shows that—

106	grams of $\text{Na}_2\text{CO}_3$	are obtained from	168 gm. $\text{NaHCO}_3$ .
$\therefore \frac{106}{20} = \frac{53}{10}$	"	"	"
			$\frac{168}{20} = 8.4$ grams
			of bicarbonate.

**Method of procedure:**

Weigh out into a dish about 9 grams of  $\text{NaHCO}_3$ , place on a fireclay triangle, and heat gently over a clear Bunsen flame until, on cooling in a desiccator and weighing, the weight is constant.

When the weight is constant, keep the dish on the balance pan, and, by removing small quantities with a spatula on to a watch-glass, adjust the weight in the dish exactly to 8.4 grams. Dissolve this quantity in distilled water, and make up to 100 c.c. in a 100 c.c. measuring flask. NOTE:—Thoroughly shake after making up to the required volume by stoppering the flask and then inverting it a few times, so as to make the solution homogeneous.

Instead of preparing a normal solution one might somewhat more conveniently prepare a semi-normal  $\left(\frac{N}{2}\right)$  or deci-normal solution  $\left(\frac{N}{10}\right)$ . From this single normal solution one could readily prepare standard solutions of acids and alkalis of any required strength.

**e. g. Preparation of Normal Hydrochloric Acid.**

Take the specific gravity of the concentrated hydrochloric acid on the bench by means of a hydrometer. It will be found to be approx. 1.16 at  $15^\circ\text{C}$ . Looking up a table giving the weights of HCl in solution corresponding to different specific gravities, one finds the percentage of acid present to be 32.2 per cent. (approx.). Now N. HCl contains 36.5 grams per litre. The volume of conc. hydrochloric acid containing 36.5 grams would be

$100 \times \frac{36.5}{32.2} = 113.4$  c.c. Take say 115–120 c.c. and dilute up to

a litre with water in a measuring flask. Shake thoroughly, and then find the exact strength by titration against the normal carbonate. Remove say 50 c.c. for this purpose, leaving 950 c.c. in the flask. Suppose that one found that 19.8 c.c. HCl were required to neutralize 20 c.c. of normal sodium carbonate. The HClAq is obviously the stronger since less of it is required. Every 19.8 c.c. should be diluted to 20 c.c. to make it normal. The residual volume of HCl, viz. 950 c.c., should therefore be

diluted until it occupies  $950 \times \frac{20}{19.8} = 959.6$  c.c.

Add 9.6 c.c. to the 950 c.c. in the flask, shake, and titrate again against the carbonate solution. 20 c.c. HCl should now be found, equivalent to 20 c.c.  $\text{Na}_2\text{CO}_3$ . Remove to a bottle, and label as N. HCl.

**Standard Sulphuric and Standard Nitric Acid** could be prepared by exactly similar methods. In the case of the sulphuric acid one could readily prove its normal character by a gravimetric estimation of the quantity present in a certain volume. The gravimetric estimation would be exactly similar to the estimation of barium already described. One would acidify strongly, boil, add  $\text{BaCl}_2\text{Aq}$  as long as a precipitate formed, filter, and weigh the  $\text{BaSO}_4$  thrown down.

**Semi-normal or deci-normal** solutions could, of course, be prepared from the normal solutions; e.g. to make a  $\frac{N}{10}$  solution of HCl after preparation of the N solution, one has merely to take 100 c.c. N solution and dilute to a litre.

**Standard Oxalic Acid** could be made direct by weighing out 63 grams of freshly crystallized oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , dissolving in water, and making up to a litre.

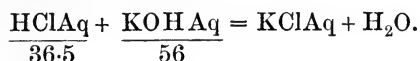
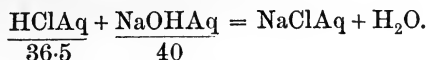
**Standard Caustic Soda and Standard Caustic Potash** could be prepared by weighing out rather more of the solids than would be necessary to give a normal solution, making solutions of approximately the strength required, and then titrating against one of the standard acids prepared from the standard carbonate, or the solution might be titrated directly against the oxalic acid.

#### METHOD OF DETERMINING THE STRENGTH OF A SOLUTION OF ACID OR ALKALI, GIVEN A SOLUTION OF KNOWN STRENGTH.

**Example I.** Given standard Normal HCl to find the strength of a solution of Caustic Soda.

The fundamental fact which one should always keep in view in determinations of this type could be stated as follows:—Normal solutions of acids and alkalies are always equivalent to each other, e.g. any given volume of N,  $\frac{N}{2}$ , or  $\frac{N}{10}$  acid is neutralized by the same volume of N,  $\frac{N}{2}$ , or  $\frac{N}{10}$  NaOH or KOH respectively.

This statement could readily be proved from the equations expressing the reaction :—



From these equations it is obvious that 36.5 grams of HCl are neutralized by 40 grams of NaOH and 56 grams of KOH. But the three quantities mentioned are those present in 1 litre of N solution.  $\therefore$  1000 c.c. of N. HCl is neutralized by 1000 c.c. N. NaOH or N. KOH.

#### METHOD OF PROCEDURE IN ABOVE CASE.

Place in a porcelain dish or conical flask 10–25 c.c. of the caustic soda solution, add a few drops of litmus or methyl orange to act as indicator, and then slowly run in from the burette the standard hydrochloric acid until the neutralization point is reached as indicated by change of tint to reddish violet or orange. Note the volume used. Carry out a check experiment, and if the volume required in the second case is identical or within 0.1 c.c. of the previous one, take a mean of the two results. If there be a greater difference than 0.1 c.c., repeat.

#### Special Notes regarding Manipulative Details.

(1) In taking 10–25 c.c. of the caustic soda solution preferably use a pipette which has been tested regarding the proper method which must be followed to ensure delivery of the volume recorded upon it. The test can be made by drawing up distilled water by suction until the level is above the graduation mark, closing the top of the tube with the thumb, and allowing the water to run out until the bottom of the meniscus reaches the graduation mark: then allow the water to flow into a small dry weighing bottle, the weight of which is known, draining the pipette at the end by putting its tip against the inside of the bottle for a few seconds and then blowing once. Knowing the density of water for the particular temperature (at 15° C. take density of water as 0.998), calculate the actual volume of water delivered from the weight found, and if the volume is appreciably more than the graduation value repeat the experiment, but merely drain the pipette as before and do not blow.

(2) Use only a small quantity of indicator, so that the tint is not darker than that of the bench solution of potassium ferrocyanide. e. g. Do not use more than one or two drops of a moderately strong solution of **methyl orange**, which should be transferred by dropping from a rod or pipette and not by pouring.

(3) In filling the burette with acid proceed as follows:— After washing the burette with water (if necessary), add a few

c.c. of the acid solution to be used, close the top with the thumb, invert a few times, and run off completely. Then fill up the burette a few c.c. beyond the top mark. On allowing the liquid to run out until the bottom of the meniscus just reaches the graduation mark, the space beyond the stopcock becomes filled with acid, which is essential, as one is measuring volume by difference as indicated by the position of the meniscus. Record the re-

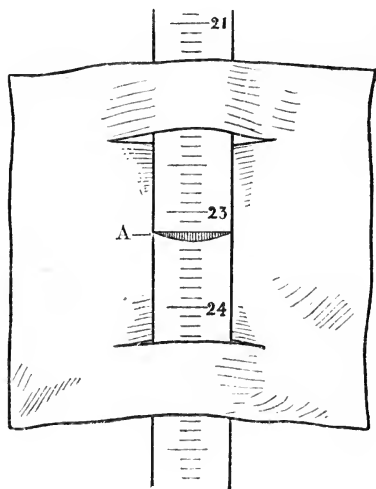


FIG. 19. METHOD OF READING POSITION OF LIQUID IN A BURETTE. The reading here would be 23.30. A, Meniscus.

sult to  $\frac{1}{100}$  of a c.c. By putting a piece of paper or card behind the meniscus,

as indicated in the diagram, a better reading may be obtained.

(4) Avoid error of **parallax** by having the eye horizontally opposite the graduation which is being read. A convenient arrangement is indicated in Fig. 19.

(5) In running the liquid from the burette, the tap should be controlled by the thumb and first two fingers of the left hand, which is passed round behind the burette as indicated in the diagram. The tap (which should be carefully smeared when dry with a very small quantity of vaseline) is gently pressed inwards, and by proper manipulation one can run in the liquid at moderate speed, and yet stop exactly as required. The right hand is used either for stirring the liquid, if placed in a beaker or porcelain basin, or for shaking the vessel if a conical flask

(Erlenmeyer) is employed. The exact method of procedure is indicated in Fig. 20.

**General Notes:**

(a) With regard to the most suitable indicator to employ, methyl orange is the best if any carbonate is likely to be present, as it is unaffected by dissolved carbonic acid. Carbonate in small quantity is nearly always present in solutions of sodium or potassium hydroxide.

Litmus can be used if the solution is boiled towards the end of the reaction, so as to decompose dissolved carbonic acid, which colours the litmus red.

(b) If there is a great discrepancy between the respective volumes of the acid and alkali required for mutual neutralization, e.g. if more than 100 c.c. of acid is required for 10 c.c. of caustic soda, or (and this is more important) if less than 2 c.c. of acid is required for 10 c.c. of soda, it is advisable to dilute one or other to (say) a tenth its former strength, so as to make the solutions more nearly equivalent to each other.

(c) It often saves time to carry out first an approximate experiment, and then two accurate determinations.

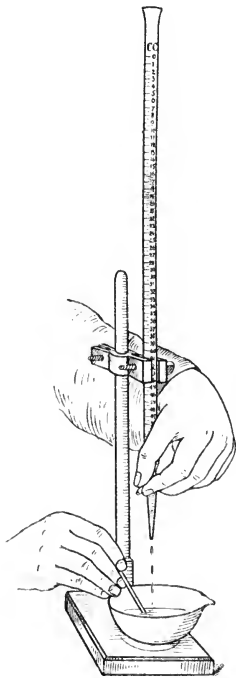


FIG. 20. METHOD OF DELIVERY OF LIQUID FROM BURETTE IN VOLUMETRIC WORK.

### METHOD OF CALCULATING RESULTS OF EXPERIMENTS.

The student should be able to record his results in three ways:

- (1) As a fraction of normal.
- (2) In grams per litre.
- (3) As a percentage, which generally means grams per 100 c.c.

A few concrete examples will make the methods of calculation clear.

**Case 1.** 20 c.c. NaOH were neutralized by 10 c.c. N. HCl.

As the strength of a solution must be inversely as the volume required for a reaction, the caustic soda solution is the weaker ;

$$20 \text{ c.c. NaOH} \equiv 10 \text{ c.c. N. HCl.}$$

$$1 \text{ c.c. NaOH} \equiv \frac{10}{20} \text{ c.c. N. HCl.}$$

i.e. the caustic soda solution is half as strong as the acid, or  $\frac{N}{2}$ .

But normal caustic soda contains 40 grams per litre (p. 231).

$\therefore$  the strength of the solution  $= \frac{40}{2} = 20$  grams per litre.

**Rule.**

Let  $x$  = vol. of N. HCl used, and 20 c.c. = vol. of NaOH taken. Then the strength of NaOH solution  $= \frac{x}{20} N$ .

More generally—

Let  $x$  = vol. of N solution used, and  $y$  = vol. of solution to be estimated taken.

Then the strength required  $= \frac{x}{y} N$ .

If  $\frac{N}{2}$  or  $\frac{N}{10}$  acid be used, the strength required becomes  $\frac{x}{y} \frac{N}{2}$  or  $\frac{x}{y} \frac{N}{10}$  respectively.

It is advisable not to use formulae like these, but to work from first principles as indicated below.

**Case 2.**

Given N. NaOH, to find the strength of the solution of HCl supplied.

Results :—

$$(1) 20 \text{ c.c. N. NaOH} \equiv 18.2 \text{ c.c. HCl.}$$

$$(2) 20 \text{ c.c. N. NaOH} \equiv 18.3 \text{ c.c. HCl.}$$

$$\text{Mean result } 20 \text{ c.c. N. NaOH} \equiv \frac{18.2 + 18.3}{2} = 18.25 \text{ c.c. HCl.}$$



**Method I.**

The acid is evidently the stronger in the proportion of 20 to 18.25,

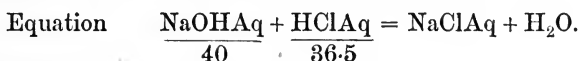
∴ its strength must be  $\frac{20}{18.25}$  N.

But a normal solution of HCl contains 36.5 grams,

∴ the strength of the acid =  $\frac{20}{18.25} \times \frac{36.5}{1} = 40$  grams per litre.

**Method II.**

It is always advisable for the beginner to check his results determined as above by another calculation from the fundamental equation expressing the reaction carried out.



Here 20 c.c. N. NaOH were taken.

1000 c.c. N. NaOH contain 40 grams.

∴ 1 c.c. N. „ contains  $\frac{40}{1000}$  gram.

and 20 c.c. N. „ contain  $\frac{40 \times 20}{1000} = \frac{8}{10}$  gram.

The equation shows that

40 grams NaOH  $\equiv$  36.5 grams HCl.

∴ 1 gram NaOH  $\equiv \frac{36.5}{40}$  „ „

and  $\frac{8}{10}$  „ NaOH  $\equiv \left( \frac{36.5}{40} \times \frac{8}{10} \right)$  grams HCl,

which must be the weight of HCl in the volume neutralized by the 20 c.c. N. NaOH, viz. in 18.25 c.c.

If 18.25 c.c. contain  $\left( \frac{36.5}{40} \times \frac{8}{10} \right)$  grams HCl, the weight in 1000 c.c. would be

$$\frac{1000}{18.25} \times \left( \frac{36.5}{40} \times \frac{8}{10} \right) = 40 \text{ grams. (Cf. Method I.)}$$

**Case 3.**

Given  $\frac{\text{N}}{10}$   $\text{H}_2\text{SO}_4$ , to find the strength of a solution of  $\text{KOH}_{\text{Aq}}$ .

Results:—

(1) 20 c.c. KOH were neutralized by 14.05 c.c.  $\frac{N}{10}$   $H_2SO_4$ .

(2) 20 c.c. KOH „ „ „ 13.95 c.c.  $\frac{N}{10}$   $H_2SO_4$ .

Mean result :

20 c.c. KOH were neutralized by  $\frac{14.05 + 13.95}{2} = 14$  c.c.  $\frac{N}{10}$   $H_2SO_4$ .

### Method I.

The KOH is evidently weaker than the acid in the proportion of 14 to 20,

$$\therefore \text{strength of KOH} = \frac{14}{20} \times \frac{N}{10}.$$

But N. KOH contains 56 grams per litre (p. 231),

$\therefore$  strength of potash

$$\begin{aligned} & \frac{7}{10} \times \frac{56}{10} = \frac{392}{100} = 3.92 \text{ grams per litre.} \end{aligned}$$

### Method II.

$$\text{Equation: } \frac{2KOH \text{Aq}}{\frac{2 \times 56}{112}} + \frac{H_2SO_4 \text{Aq}}{\frac{2 + 32 + 64}{98}} = K_2SO_4 \text{Aq} + 2H_2O.$$

(a) Find weight of substance in volume of standard solution taken.

$$1000 \text{ c.c. } \frac{N}{10} H_2SO_4 \text{ contains } \frac{49}{10} = 4.9 \text{ grams.}$$

$$1 \text{ c.c. } \frac{N}{10} \text{ „ „ } \frac{4.9}{1000} \text{ grams.}$$

$$14 \text{ c.c. } \frac{N}{10} \text{ „ „ } \left( \frac{4.9}{1000} \times \frac{14}{1} \right) \text{ grams.}$$

(b) Find the weight of substance in the volume of solution neutralized by standard.

From equation

$$98 \text{ grams } H_2SO_4 \equiv 112 \text{ grams KOH.}$$

$$\therefore 1 \text{ gram } H_2SO_4 \equiv \frac{112}{98} \text{ „ „}$$

And  $\frac{4.9 \times 14}{1000}$  grams  $\text{H}_2\text{SO}_4 \equiv \left(\frac{112}{98} \times \frac{4.9 \times 14}{1000}\right)$  grams KOH,

which must be the weight of potash in the volume neutralized, viz. in 20 c.c.

(c) Find the strength in grams per litre.

20 c.c. contain  $\left(\frac{112}{98} \times \frac{4.9 \times 14}{1000}\right)$  grams KOH.

$\therefore$  1000 c.c.     „      $\frac{1000}{20} \times \frac{112}{98} \times \frac{4.9 \times 14}{1000} = 3.92$  grams KOH.  
(Cf. Method I.)

#### Case 4.

The strength of standard acid or alkali is not given as a fraction of normal, but in grams per litre.

E.g. Find the strength of a solution of KOH, 20 c.c. of which are neutralized by 15 c.c. of  $\text{HNO}_3$ , containing 30 grams of the acid per litre.

#### Method I.

Transform the strength of acid into fraction of normal. In this case N.  $\text{HNO}_3$  contains 63 grams per litre,

$\therefore$  30 grams per litre =  $\frac{30}{63}$  N.

If 20 c.c. KOH  $\equiv$  15 c.c.  $\frac{30}{63}$  N.  $\text{HNO}_3$

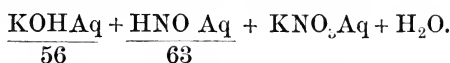
the strength of the KOH =  $\frac{15}{20} \times \frac{30}{63}$  N.

But N. KOH contains 56 grams per litre,

$\therefore$  strength =  $\frac{15}{20} \times \frac{30}{63} \times \frac{56}{1} = 20$  grams per litre.

#### Method II.

Calculate direct from equation as before—



1000 c.c.  $\text{HNO}_3$  contain 30 grams per litre,

$\therefore$  1 c.c.     „     contains  $\frac{30}{1000}$  grams

$\therefore$  15 c.c.     „     contain  $\left(\frac{30 \times 15}{1000}\right)$  grams.

Equation shows that

$$\begin{aligned}
 & 63 \text{ grams HNO}_3 \text{ will neutralize } 56 \text{ grams KOH,} \\
 \therefore & 1 \text{ gram HNO}_3 \text{ " " } \frac{56}{63} \text{ " " } \\
 \text{and } & \frac{30 \times 15}{1000} \text{ gm. HNO}_3 \text{ " " } \frac{56}{63} \times \frac{30 \times 15}{1000} \text{ gm. KOH.} \\
 & = \text{weight of KOH in 20 c.c.}
 \end{aligned}$$

$\therefore$  strength of KOH in grams per litre

$$= \frac{1000}{1000} \times \frac{56}{63} \times \frac{30 \times 15}{1000} = 20 \text{ grams.}$$

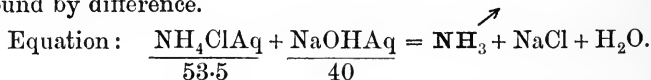
Note. 20 grams per litre would be a 2 per cent. solution.

### Indirect Determinations.

A great many indirect determinations can be made by using standard acid and alkali. The following are interesting types:—

**I. Determination of strength of a given solution of an Ammonium Salt** (e.g. ammonium chloride), given standard caustic soda and standard acid.

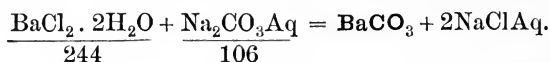
**Method.** Boil up a certain volume of the solution of ammonium salt in a porcelain basin with a measured volume of NaOH Aq in excess until ammonia ceases to be evolved. Calculate how much NaOH is still present by adding litmus or methyl orange, and titrating against standard acid until neutral. Knowing the weight of NaOH taken, the quantity used up can be found by difference.



From the equation it is obvious that 40 grams of NaOH are required to decompose 53.5 grams of  $\text{NH}_4\text{Cl}$ .

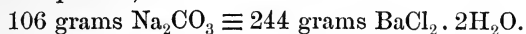
**II. Determination of strength of a given solution of Barium Chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) by precipitation of the metal as Carbonate with standard Sodium Carbonate solution.** Standard acid is also supplied.

**Method.** To a measured volume of the given solution add a certain volume of the standard  $\text{Na}_2\text{CO}_3$ , more than enough to completely precipitate the metal as indicated in the equation:



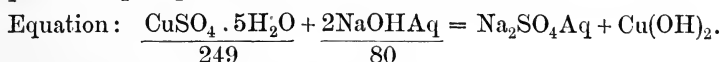
Filter and wash thoroughly, collecting the filtrate and wash water in a beaker or porcelain basin. Add methyl orange and titrate the excess of carbonate (which will of course be in the filtrate) against standard acid.

From the equation,



**III. Determination of strength of a given solution of Copper Sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) by two methods:**

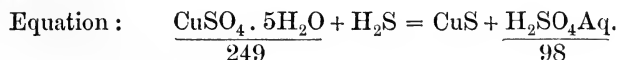
(a) **By precipitation of the Copper as Hydroxide with standard NaOH.** Add a known volume of standard NaOH in excess to a measured volume of the solution of copper sulphate. Boil. Filter, wash and titrate filtrate and washings against standard acid, so as to estimate how much NaOH has been required for precipitation.



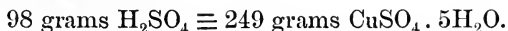
From equation, 80 grams NaOH  $\equiv$  249 grams  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

(b) **By precipitation of Copper as Sulphide.**

Pass washed  $\text{H}_2\text{S}$  gas through a measured volume of the copper sulphate until precipitation is complete. Filter, wash, boil off the dissolved  $\text{SH}_2$ , and titrate the sulphuric acid formed during the reaction against standard caustic soda, using a suitable indicator (e. g. litmus).



Equation shows that



In either case (*a* or *b*) the filtration and washing can be avoided by precipitating in a graduated flask, say 200 cc. Cool, dilute with water to the mark, shake well, and allow to settle. Then pipette out 100 cc. of the clear liquid and titrate, and multiply the result by 2.

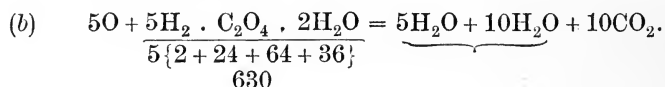
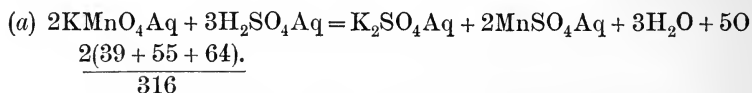
### ESTIMATION OF OXALIC ACID BY MEANS OF STANDARD POTASSIUM PERMANGANATE.

Oxalic acid is very slowly oxidized by potassium permanganate at ordinary temperature, but almost immediately at about 60° C.

**Method.** Take 10–25 c.c. of the oxalic acid solution, add about an equal bulk of dilute sulphuric acid, heat to 60°–70° C., and add the standard permanganate solution from a burette until the reaction mixture is tinted a faint pink. Note the volume.

**Precaution.** A sufficiency of sulphuric acid must be present or brown oxide of manganese is precipitated.

Calculate the strength of the oxalic acid solution, taking into consideration the following relationships. The equations expressing the reaction might be stated as follows:—



It follows from these equations that



i. e. 316 grams  $\text{KMnO}_4$  would oxidize 630 grams of crystallized oxalic acid.

A normal solution of an oxidizing agent is, it must be remembered, of such a strength as will give up 8 grams of Oxygen per Litre.

But 316 grams of  $\text{KMnO}_4$ , as Equation (a) shows, can give up 80 grams of oxygen to an oxidizable body.

$\therefore$  a normal solution of  $\text{KMnO}_4$  should contain  $\frac{316}{10} = 31.6$  grams per litre, and, as 316 grams  $\text{KMnO}_4$  can completely oxidize 630 grams  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , 31.6 grams of  $\text{KMnO}_4$  will oxidize 63 grams  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , which is the weight of oxalic acid in a normal solution. Normal  $\text{KMnO}_4$  and N.  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  are therefore equivalent to each other, and calculations of strength can be made as in acidimetry and alkalimetry.

**Case 1.** The standard permanganate given is  $\frac{N}{10}$ , i. e. it contains 3.16 grams per litre.

25 c.c. oxalic acid are oxidized by 37.5 c.c.  $\frac{N}{10}$   $\text{KMnO}_4$ .

**Method I.** The oxalic acid is the stronger in the proportion of 37.5 to 25, since strength is inversely proportional to volume required as already noted (p. 240).

$$\therefore \text{strength of oxalic acid} = \frac{37.5}{25} \times \frac{N}{10}.$$

But N. oxalic acid contains 63 grams per litre.

$$\therefore \text{strength of oxalic acid} = \frac{37.5}{25} \times \frac{63}{10} = 9.45 \text{ grams per litre.}$$

**Method II.** Check this result by an analogous method to that used in acidimetry and alkalimetry.

1000 c.c.  $\frac{N}{10}$   $\text{KMnO}_4$  contain 3.16 grams.

$\therefore$  1 c.c.  $\frac{N}{10}$  " contains  $\frac{3.16}{1000}$  "

$\therefore$  37.5 c.c.  $\frac{N}{10}$  " contain  $\left(\frac{3.16 \times 37.5}{1000}\right)$  grams.

From equations:

316 grams  $\text{KMnO}_4 \equiv 630$  grams oxalic acid.

$\therefore$  1 gram "  $\equiv \frac{630}{316}$  " " "

$\therefore \frac{3.16 \times 37.5}{1000}$  "  $\equiv \frac{630}{316} \times \frac{3.16 \times 37.5}{1000}$

= weight of oxalic acid in 25 c.c.

$\therefore$  strength of oxalic acid in grams per litre

$$= \frac{1000}{25} \times \frac{630}{316} \times \frac{3.16 \times 37.5}{1000} = 9.45 \text{ grams.}$$

**Case 2.** The strength of the permanganate is not given as fraction of normal, but as 5 grams per litre.

**Result** :—20 c.c.  $\text{KMnO}_4 \equiv 30$  c.c. oxalic acid.

**Method I.** Calculation from fraction of normal.

N.  $\text{KMnO}_4$  contains 31.6 grams per litre.

$$\therefore \text{strength in this case} = \frac{5}{31.6} \text{ N.}$$

Hence the strength of the oxalic acid  $= \frac{20}{30} \times \frac{5}{31.6} \text{ N.}$

And N. oxalic contains 63 grams per litre.

$$\therefore \text{ strength} = \frac{20}{30} \times \frac{5}{31.6} \times \frac{63}{1} = 6.64 \text{ grams per litre (approx.).}$$

**Method II.** Calculation from equations.

1000 c.c.  $\text{KMnO}_4$  contain 5 grams.

1 c.c. „ contains  $\frac{5}{1000}$  grams.

20 c.c. „ contain  $\frac{5 \times 20}{1000}$  grams  $= \frac{1}{10}$  gram.

From equations

316 grams  $\text{KMnO}_4 \equiv 630$  grams oxalic acid.

1 gram „  $\equiv \frac{630}{316}$  „ „ „

$\frac{1}{10}$  „ „  $\equiv \frac{630}{316} \times \frac{1}{10}$  grams oxalic acid.

$=$  weight of oxalic acid in 30 c.c.

$\therefore$  strength of the oxalic acid in grams per litre

$$= \frac{1000}{30} \times \frac{630}{316} \times \frac{1}{10} = 6.64 \text{ grams.}$$



### ESTIMATION OF CHLORIDES VOLUMETRICALLY BY STANDARD SILVER NITRATE, USING POTASSIUM CHROMATE AS INDICATOR.

**Method.** To a measured volume of the chloride solution, which must be neutral, add a few drops of potassium chromate, and then add silver nitrate from a burette until a faint reddish tint appears, due to the formation of silver chromate. This only happens after complete precipitation of the chloride, as silver chromate is decomposed by solutions of chlorides to give silver chloride.

**A. Estimation of strength of Potassium Chloride solution** (cf. p. 224).

$$20 \text{ c.c. KCl} \equiv 10 \text{ c.c. } \frac{N}{10} \text{ AgNO}_3.$$

$$\therefore \text{ strength of KCl} = \frac{10}{20} \times \frac{N}{10} = \frac{N}{20}.$$

But N. KCl contains  $(39 + 35.5) = 74.5$  grams per litre.

$$\begin{aligned} \therefore \text{ strength of KCl in grams per litre} \\ = \frac{74.5}{20} = 3.73 \text{ grams (approx.).} \end{aligned}$$

**B. Estimation of strength of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$**  (cf. p. 226).

Proceed as above, but add  $\text{K}_2\text{CrO}_4$  until solution is tinted yellow, i. e. until all barium is precipitated as chromate.

$$25 \text{ c.c. BaCl}_2 \cdot 2\text{H}_2\text{O in solution} \equiv 40 \text{ c.c. } \frac{N}{10} \text{ AgNO}_3.$$

$$\text{Strength of BaCl}_2 \cdot 2\text{H}_2\text{O} = \frac{40}{25} \times \frac{N}{10}.$$

$$\text{But N. BaCl}_2 \cdot 2\text{H}_2\text{O would contain } \frac{\text{Mol. wt.}}{2} = \frac{244}{2} = 122.$$

$$\begin{aligned} \therefore \text{ strength of barium chloride solution} \\ = \frac{40}{25} \times \frac{122}{10} = 19.52 \text{ grams per litre.} \end{aligned}$$



TABLE OF ATOMIC WEIGHTS (1909).

The values are given to the second decimal place where known. O = 16.

Element.	Symbol.	Atomic Weight. O = 16.		Element.	Symbol.	Atomic Weight. O = 16.	
		Accurate Values.	Useful Approximations.			Accurate Values.	Useful Approximations.
Aluminium	Al	27.1	27	Molybdenum	Mo	96.0	
Antimony	Sb	120.2	120	Neodymium	Nd	144.3	
Argon	A	39.9		Neon	Ne	20.0	
Arsenic	As	75.0	75	Nickel	Ni	58.68	
Barium	Ba	137.37	137	Nitrogen	N	14.01	14
Bismuth	Bi	208.0	208	Osmium	Os	190.9	
Boron	B	11.0	11	Oxygen	O	16.0	16
Bromine	Br	79.92	80	Palladium	Pd	106.7	
Cadmium	Cd	112.40		Phosphorus	P	31.0	31
Cæsium	Cs	132.81		Platinum	Pt	195.0	
Calcium	Ca	40.09	40	Potassium	K	39.10	39
Carbon	C	12.0	12	Praseodymium	Pr	140.6	
Cerium	Ce	140.25		Radium	Ra	226.4	
Chlorine	Cl	35.46	35.5	Rhodium	Rh	102.9	
Chromium	Cr	52.1	52	Rubidium	Rb	85.45	
Cobalt	Co	58.97		Ruthenium	Ru	101.7	
Columbium	Cb	93.5		Samarium	Sa	150.4	
Copper	Cu	63.57	63.6	Scandium	Sc	44.1	
Dysprosium	Dy	162.5		Selenium	Se	79.2	
Erbium	Er	167.4		Silicon	Si	28.3	
Europium	Eu	152.0		Silver	Ag	107.88	108
Fluorine	F	19.0	19	Sodium	Na	23.0	23
Gadolinium	Gd	157.3		Strontium	Sr	87.62	
Gallium	Ga	69.9		Sulphur	S	32.07	32
Germanium	Ge	72.5		Tantalum	Ta	181.0	
Glucinum or } Beryllium }	Gl	9.1		Tellurium	Te	127.5	
Gold	Au	197.2		Terbium	Tb	159.2	
Helium	He	4.0		Thallium	Tl	204.0	
Hydrogen	H	1.008	1	Thorium	Th	232.42	
Indium	In	114.8		Thulium	Tm	168.5	
Iodine	I	126.92	127	Tin	Sn	119.0	119
Iridium	Ir	193.1		Titanium	Ti	48.1	
Iron	Fe	55.85	56	Tungsten	W	184.0	
Krypton	Kr	81.8		Uranium	U	238.5	
Lanthanum	La	139.0		Vanadium	V	51.2	
Lead	Pb	207.10	207	Xenon	Xe	128.0	
Lithium	Li	7.0		Ytterbium } (Neoytterbium) }	Yb	172.0	
Lutecium	Lu	174.0		Yttrium	Y	89.0	
Magnesium	Mg	24.32	24	Zinc	Zn	65.37	65
Manganese	Mn	54.93	55	Zirconium	Zr	90.6	
Mercury	Hg	200.0	200				

NOTE.—The elements in thick type are important for practical or theoretical reasons, or both.

# WEIGHTS AND MEASURES. IMPERIAL (OR BRITISH) AND METRIC SYSTEMS.

## I. IMPERIAL (OR BRITISH) SYSTEM.

### Length.

Smallest unit:—inch.      12 in.=1 foot.      3 ft.=1 yard.      1760 yards=1 mile.

(Note.—A halfpenny is 1 inch in diameter.)

### Avoirdupois Weight.

Smallest unit:—

drachm.      16 dr.=1 ounce.      16 oz.=1 pound (lb.).      112 lb.=1 cwt.      20 cwt.=1 ton.  
Grains 27.3      437.5      7000

### Troy Weight (for Gold, Silver, and Platinum).

Smallest unit:—grain.      24 gr.=1 pennyweight (dwt.).      20 dwt.=1 ounce.      12 oz.=1 lb.  
Grains      1      24      480      5760

### Diamond and Pearl Weight.

Smallest unit:—grain.      4 gr.=1 carat.      150 carats=1 ounce Troy.  
Grains (Troy)      0.8      3.2      480

### Apothecaries' Weight (for Prescriptions).

Smallest unit:—grain.      20 gr.=1 scruple.      3 scr.=1 drachm.      8 dr.=1 ounce.      12 oz.=1 lb.  
Grains (Apoth. or Troy)      1      20      60      480      5760

### Apothecaries' Fluid Measure.

Smallest unit:—Minim.      60 min.=1 dr.      8 dr.=1 oz.      20 oz.=1 pint.      8 pints=1 gall.  
Vol. at 62°F. }      0.91 grain      54.7      437.5      8750      70000  
occupied by }      of water.      gr. water.      gr. water.      gr. water.      gr. water.

## II. METRIC SYSTEM.

**Mass**      1 gramme=weight of 1 cubic centimetre (c. c.) of dist. water at 4°C.  
(usually written gram).

1 kilogram = 1000 grammes	}	Note.—Greek prefixes multiply. Latin prefixes divide.
1 decigram = $\frac{1}{10}$ gramme		
1 centigram = $\frac{1}{100}$ gramme		
1 milligram = $\frac{1}{1000}$ gramme		

**Capacity**      1 cubic centimetre (c. c.)=Vol. occupied by 1 gram of water at 4°C.  
1 litre=1000 c. c.

### Length

1 metre  
1000 metres = 1 kilometre.  
1 decimetre =  $\frac{1}{10}$  metre.  
1 centimetre =  $\frac{1}{100}$  metre.  
1 millimetre =  $\frac{1}{1000}$  metre.

## III. RELATION OF IMPERIAL STANDARDS TO METRIC.

- a) **Mass**      1 ounce=28.35 grams.      1 lb.=453.6 grams (approx.).
- b) **Capacity**      1 minim=0.059 c. c. [practically 1 drop (approx.).]  
                          1 fluid drachm=3.552 c. c.  
                          1 fluid ounce=28.42 c. c.  
                          1 pint=568.34 c. c. (rather more than  $\frac{1}{2}$  litre).  
                          1 gallon=4.546 litres.
- c) **Length**      1 inch=2.54 centimetres (cm.).  
                          1 foot=30.48 centimetres.  
                          1 yard=0.9144 metre (approx.).

## IV. RELATION OF METRIC STANDARDS TO IMPERIAL.

**Length**      1 metre = 39.37 inches.  
**Capacity**      1 litre = 1.76 pints.      1 c. c. = 16.9 minims.  
**Mass**      1 gramme = 15.432 grains.      1 kilogramme = 2 lb. 3 oz. 119.86 grains (approx.).

Scale divided in inches (above) and centimetres (below).

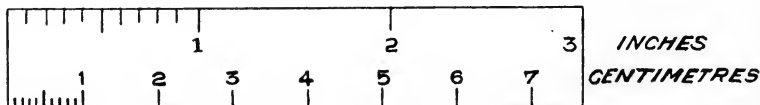


TABLE OF ATOMIC WEIGHTS (1909).

The values are given to the second decimal place where known. O = 16.

Element.	Symbol.	Atomic Weight. O = 16.		Element.	Symbol.	Atomic Weight. O = 16.	
		Accurate Values.	Useful Approximations.			Accurate Values.	Useful Approximations.
Aluminium	Al	27.1	27	Molybdenum	Mo	96.0	
Antimony	Sb	120.2	120	Neodymium	Nd	144.3	
Argon	A	39.9		Neon	Ne	20.0	
Arsenic	As	75.0	75	Nickel	Ni	58.68	
Barium	Ba	137.37	137	Nitrogen	N	14.01	14
Bismuth	Bi	208.0	208	Osmium	Os	190.9	
Boron	B	11.0	11	Oxygen	O	16.0	16
Bromine	Br	79.92	80	Palladium	Pd	106.7	
Cadmium	Cd	112.40		Phosphorus	P	31.0	31
Cæsium	Cs	132.81		Platinum	Pt	195.0	
Calcium	Ca	40.09	40	Potassium	K	39.10	39
Carbon	C	12.0	12	Praseodymium	Pr	140.6	
Cerium	Ce	140.25		Radium	Ra	226.4	
Chlorine	Cl	35.46	35.5	Rhodium	Rh	102.9	
Chromium	Cr	52.1	52	Rubidium	Rb	85.45	
Cobalt	Co	58.97		Ruthenium	Ru	101.7	
Columbium	Cb	93.5		Samarium	Sa	150.4	
Copper	Cu	63.57	63.6	Scandium	Sc	44.1	
Dysprosium	Dy	162.5		Selenium	Se	79.2	
Erbium	Er	167.4		Silicon	Si	28.3	
Europium	Eu	152.0		Silver	Ag	107.88	108
Fluorine	F	19.0	19	Sodium	Na	23.0	23
Gadolinium	Gd	157.3		Strontium	Sr	87.62	
Gallium	Ga	69.9		Sulphur	S	32.07	32
Germanium	Ge	72.5		Tantalum	Ta	181.0	
Glucium or } Beryllium }	Gl	9.1		Tellurium	Te	127.5	
Gold	Au	197.2		Terbium	Tb	159.2	
Helium	He	4.0		Thallium	Tl	204.0	
Hydrogen	H	1.008	1	Thorium	Th	232.42	
Indium	In	114.8		Thulium	Tm	168.5	
Iodine	I	126.92	127	Tin	Sn	119.0	119
Iridium	Ir	193.1		Titanium	Ti	48.1	
Iron	Fe	55.85	56	Tungsten	W	184.0	
Krypton	Kr	81.8		Uranium	U	238.5	
Lanthanum	La	139.0		Vanadium	V	51.2	
Lead	Pb	207.10	207	Xenon	Xe	128.0	
Lithium	Li	7.0		Ytterbium } (Neoytterbium)	Yb	172.0	
Lutecium	Lu	174.0		Yttrium	Y	89.0	
Magnesium	Mg	24.32	24	Zinc	Zn	65.37	65
Manganese	Mn	54.93	55	Zirconium	Zr	90.6	
Mercury	Hg	200.0	200				

NOTE.—The elements in thick type are important for practical or theoretical reasons, or both.

## MEMORANDA

## MEMORANDA

## MEMORANDA



## MEMORANDA

## MEMORANDA

# INDEX

A.  
 Acetates, 186, 193, 207, 209.  
 Acid, Definition, 21.  
 Acid, Acetic, 185, 193.  
     Arsenic, 185, 203.  
     Arsenious, 185, 202.  
     Boracic, 44, 65.  
     Carbonic, 185, 186, 190.  
     Hydriodic, 38, 185, 199.  
     Hydrobromic, 37, 185, 198.  
     Hydrochloric, 37, 185, 197.  
     Hydrocyanic, 186, 192.  
     Iodic, 33.  
     Metastannic, 34.  
     Nitric, 32, 185, 188, 200.  
         Oxidizing Action, 33.  
     Nitrous, 31, 32, 185, 186, 195.  
     Oxalic, 185, 188, 204.  
     Phosphoric, 185, 188, 201.  
     Prussic, 186, 192.  
     Silicic, 44.  
     Sulphuric, 42, 185, 186, 196.  
     Sulphurous, 41, 185, 186, 194.  
     Tartaric, 185, 188, 205.  
 Acid salts, 50.  
 Acidimetry, 234.  
 Acids—interaction with Oxides, 51,  
     52, 59, 61.  
     Actions on Metals, 33, 37, 42.  
 Air, 27.  
 Alkalies, 21.  
 Alkalimetry, 234.  
 Alum, Ammonia, 56, 68.  
     Potash, 56, 68.  
 Aluminium, 115.  
     Bronze, 115.  
     Carbide, 115.  
     Chloride, 115.  
     Compounds, Tests for, 114.  
     Hydroxide, 57, 70, 114, 115.  
     Oxide, 68, 115.  
     Sulphate, 115.  
     Sulphide, 114.  
 Amalgam, Sodium, 103.  
 Ammonia, 28, 132, 133.  
     Alum, 56, 68.

Ammonium Bisulphate, 133.  
     Bitartrate, 133.  
     Carbonate, 133.  
     Chloride, 56, 61, 133.  
     Compounds, Tests for, 132.  
         ,, List of, 133.  
     Hydroxide, 133.  
     Molybdate, 93, 201.  
     Nitrate, 133.  
     Nitrite, 26.  
     Oxalate, 56, 63, 133.  
     Sulphate, 133.  
     Sulphide, 133.  
     Thioantimoniate, 110.  
     Thioarsenate, 106.  
     Thiostannate, 112.  
 Analysis, Gravimetric, 223.  
     Qualitative (Kations), 145 et seq.  
         ,, (Anions), 185 et seq.  
     Volumetric, 230.  
 Anhydride, Definition, 20.  
 Anhydride, Chromic, 119.  
     Nitric, 32.  
     Nitrous, 31.  
     Phosphoric, 43.  
     Sulphuric, 42.  
     Sulphurous, 41.  
 Anion, 77.  
 Anode, 76.  
 Antimony, 111.  
     Chlorides, 111.  
     Compounds, Tests for, 110.  
         ,, List of, 111.  
     Oxides, 111.  
     Oxychloride, 110, 111.  
     Sulphate, 111.  
     Sulphide, 110, 111.  
     Tetroxide, 111.  
     Trichloride, 111.  
     Trioxide, 111.  
     Trisulphide, 110, 111.  
 Apparatus, setting up, 5.  
 Aq, meaning of Term, 17.  
 Aqua regia, 158, 167, 187.  
 Argon, 27.  
 Arithmetical Calculations, 21-24, 55,  
     226, 239.  
     Gases, Correction for Pressure, 23.

## Arithmetical Calculations :

- Gases, Correction for Temperature, 23.
- Arsenates, 188, 203, 209.
- Arsenic, 85, 106, 107, 109.
  - Compounds, Tests for, 106.
  - " List of, 109.
  - Pentasulphide, 106, 109.
  - Pentoxide, 109.
  - Sulphide, 106, 109.
  - Trichloride, 109.
  - Trioxide, 109.
- Arsenious Compounds, Tests for, 106.
- Arsenites, 188, 202, 209.
- Arseniuretted Hydrogen, 108.
- Atmosphere, 27.
- Atom, Definition, 4.
- Atomic Weights, Table of, 251.

## B.

- Barium, 125.
  - Carbonate, 124, 125.
  - Chloride, 125, 226.
  - Chromate, 119, 125.
  - Compounds, Tests for, 124.
  - " List of, 125.
  - Hydroxide, 125.
  - Nitrate, 56, 58, 125.
  - Oxide, 125.
  - Peroxide, 125.
  - Phosphate, 125.
  - Sulphate, 124, 125.
  - Sulphide, 124, 125.
- Bases, Definition, 29.
- Basic Salts, Definition, 50.
- Bell-metal, 101.
- Bismuth, 105.
  - Chloride, 105.
  - Compounds, Tests for, 104.
  - " List of, 105.
  - Hydroxide, 57, 70.
  - Oxide, 68, 105.
  - Oxychloride, 104, 105.
  - Sulphate, 105.
  - Sulphide, 104, 105.
- Bisulphate, 7.
- Borax, 56, 65.
  - " Bead Tests, 86.
- Boron, 43.
- Boyle's Law, 23.
- Brass, 101, 121.
- Braunite, 123.
- Bromides, 188, 198, 207.
- Bromine, 35.
- Bronze, 101, 121.
- Bunsen Flame, 81.
- Burette, 232.

## C.

- Calamine, 121.
- Calcium, 128.
  - Bicarbonate, 25, 39.
  - Carbonate, 128, 129.
  - Chloride, 129.
  - Chromate, 129.
  - Compounds, Tests for, 128.
  - " List of, 129.
  - Fluoride, 129.
  - Hydroxide, 57, 70, 129.
  - Oxalate, 128, 129.
  - Oxide, 129.
  - Phosphate, 129.
  - Sulphate, 128, 129.
  - Sulphide, 129.
  - Tartrate, 129.
- Calculations, 21, 24.
- Calomel, 97.
- Carbon, 38.
  - Dioxide, 39.
  - Monoxide, 38.
- Carbonates, Reactions of, 186, 190, 206.
- Carbonic Acid, 186.
- Cassiterite, 113.
- Cast Iron, 117.
- Catalytic Action, 18.
- Cathode, 76.
- Cations, 76.
- Caustic Potash, 69.
  - Soda, 57, 69.
- Celestine, 127.
- Chalk, 129.
- Charcoal, Reduction on, 84.
- Charles' Law, 23.
- Chlorides, 188, 197, 209.
  - Formulae, 6.
- Chlorine, 34.
  - Estimation, 224, 249.
- Chrome Alum, 119.
- Chromic Anhydride, 119.
  - Chloride, 119.
  - Hydroxide, 118, 119.
  - Oxide, 119.
  - Sulphate, 119.
- Chromium, 119.
  - Compounds, Tests for, 118.
  - " List of, 119.
  - Oxide, 68, 119.
- Cinnabar, 103.
- Coloured Masses, Blowpipe, 85.
- Combustion, 80.
- Compound, Definition, 3.
- Copper, 62.
  - Compounds, Tests for, 100.
  - " List of, 101.
- Corrosive Sublimate, 103.
- Crystallization, 13.
  - Water of, 53.

Cupric Chloride, 101.  
 Ferrocyanide, 100.  
 Hydroxide, 70, 100.  
 Nitrate, 101.  
 Oxide, 57, 68, 69, 101.  
 Sulphate, 52, 56, 61, 101.  
 Sulphide, 100, 101.  
 Cuprous Chloride, 56, 67, 101.  
 Iodide, 101.  
 Oxide, 57, 69, 101.  
 Cyanides, 186, 192, 207, 209.

D.

Decantation, 12.  
 Deci-normal Solutions, 231.  
 Desiccator, 225.  
 Dissociation, 75.  
 Distillation, 13.  
 Dolomite, 131.  
 Double Decomposition, 77, 78.  
 Salts, 50.  
 Dry Tests, Metals, 80.  
 Drying Oven, 227.

E.

Electrolysis, 77.  
 Electrolytes, 77.  
 Element, Definition, 3.  
 Equations, 5.  
 Evaporation, 13.

F.

Ferric Chloride, 117.  
 Compounds, Tests for, 116.  
 Hydroxide, 57, 70, 116, 117.  
 Oxide, 57, 68, 117.  
 Sulphate, 117.  
 Ferrous Carbonate, 117.  
 Chloride, 117.  
 Compounds, Tests for, 116.  
 Oxide, 117.  
 Sulphate, 54, 56, 62, 117.  
 Sulphide, 116, 117.  
 Filtration, 12.  
 Fluor-spar, 129.  
 Formulae, 5.  
 Fusible Metal, 105.

G.

Galena, 99.  
 German Silver, 101, 121.  
 Glauber's Salt, 65.  
 Gravimetric Analysis, 223.  
 Groups, Arrangement of Metals into, 141.

Gun-metal, 101.  
 Gunpowder, 3.  
 Gutzeit's Test for Arsenic, 108.  
 Gypsum, 129.

H.

Haematite, 117.  
 Hard Water, 25.  
 Henry's Law, 11.  
 Hydrogen, 14.  
 Nascent, 16.  
 Hydrogen Bromide, 37.  
 Chloride, 37.  
 Iodide, 38.  
 Phosphoretted, 43.  
 Sulphate, 42.  
 Sulphide, 39-41.  
 Hydroxide Ion, 78.  
 Hydroxides, 212.  
 Hypothesis, Ionic, 75.

I.

Incrustations, Blowpipe, 86.  
 Indicators, 234.  
 Insoluble Compounds, 171.  
 Iodides, 188, 199, 207.  
 Iodine, 36.  
 Ionic Hypothesis, 75.  
 Iron, 117.  
 Compounds, Tests for, 116.  
 „ List of, 117.  
 (See Ferric and Ferrous Compounds.)

L.

Laughing Gas, 30.  
 Law, Boyle's, 23.  
 Charles', 23.  
 Henry's, 11.  
 Lead, 59.  
 Alloys, 99.  
 Lead Acetate, 56, 63, 99.  
 Carbonate, 99.  
 Chloride, 58, 98, 99.  
 Chromate, 98, 99, 119.  
 Compounds, Tests for, 98.  
 „ List of, 99.  
 Dioxide, 99.  
 Hydroxide, 57, 70, 99.  
 Iodide, 56, 60, 98, 99.  
 Nitrate, 56, 59, 99.  
 Oxides, 68, 99.  
 Red, 99.  
 Sugar of, 99.  
 Sulphate, 98, 99.  
 Sulphide, 98, 99.  
 White, 99.  
 Lime, 20.  
 Litharge, 59, 99.  
 Litmus, 234.

## M.

- Magnalium, 115.  
 Magnesia, 131.  
 Magnesite, 131.  
 Magnesium, 131.  
     Ammon. Phosphate, 130, 131.  
     Carbonate, 130, 131.  
     Chloride, 131.  
     Compounds, Tests for, 130.  
         " List of, 131.  
     Hydroxide, 130, 131.  
     Nitride, 26.  
     Oxide, 131.  
     Sulphate, 62, 131.  
     Sulphide, 131.  
 Malachite, 101.  
 Manganese, 123.  
     Carbonate, 123.  
     Chloride, 123.  
     Compounds, Tests for, 122.  
         " List of, 123.  
     Oxides, 122, 123.  
     Sulphate, 123.  
     Sulphide, 122, 123.  
 Manganous Compounds, Tests for, 122.  
 Manipulations, General, 8.  
 Marble, 129.  
 Marsh's Test, 108.  
 Mercuric Chloride, 103.  
     Compounds, Tests for, 102.  
         " List of, 103.  
     Iodide, 56, 67, 102, 103.  
     Nitrate, 103.  
     Oxide, 57, 68, 102, 103.  
     Sulphate, 103.  
     Sulphide, 102, 103.  
 Mercurous Chloride, 96, 97.  
     Compounds, Tests for, 96.  
         " List of, 97.  
     Iodide, 96, 97.  
     Nitrate, 97.  
     Oxide, 97.  
     Sulphate, 97.  
     Sulphide, 96, 97.  
 Mercury. *See* Mercuric and Mercurous.  
 Metal, Definition, 3.  
 Metallic Salts, Preparation, 49 et sq.  
 Metals, Summary of Tests for, 94 et sq.  
 Methyl Orange, 234.  
 Metric System, 250.  
 Mixture, Definition, 3.  
 Molecule, Definition, 4.

## N.

- Nitrates, Tests for, 185, 188, 200, 208.  
 Nitric Acid, 32-34.  
     Anhydride, 32.  
     Oxide, 30.

- Nitrites, 186, 195, 207, 209.  
 Nitrogen, 26.  
     Monoxide, 30.  
     Oxides, 30.  
     Pentoxide, 32.  
     Tetroxide, 31.  
     Trioxide, 31.  
 Nitrous Anhydride, 31.  
     Oxide, 30.  
 Non-metallic Elements, 4.  
 Normal Salts, 50.  
     Solutions, 230.

## O.

- Orpiment, 109.  
 Oxalates, 185, 188, 204, 207, 209.  
     Estimation, 246.  
 Oxide, Definition, 20.  
 Oxides, 210.  
 Oxidizing Flame, 83.  
 Oxygen, 17.  
 Ozone (in air), 28.

## P.

- Permanganate, Titration with, 246.  
 Pewter, 99.  
 Phenol Phthalein, 234.  
 Phosphates, 185, 188, 201, 208, 209.  
 Phosphine (Phosphoretted Hydrogen), 43.  
 Phosphonium Compounds, 43.  
 Phosphoric Anhydride, 43.  
 Phosphorus Compounds, 43.  
     Oxides, 43.  
     Pentoxide, 43.  
 Pipette, 232.  
 Plaster of Paris, 129.  
 Platinum Wire Tests, 87.  
 Polymerism, 31.  
 Potash, Caustic, 135.  
 Potassium, 135.  
     Aluminium Sulphate, 56, 68.  
     Antimonyl Tartrate, 56, 64.  
     Bichromate, 119.  
     Bisulphate, 135.  
     Bitartrate, 134.  
     Bromide, 56, 66, 135.  
     Carbonate, 135.  
     Chlorate, 223.  
     Chloride, 135.  
     Chloroplatinate, 134.  
     Chromate, 119, 135.  
     Compounds, Tests for, 134.  
         " List of, 135.  
     Cyanide, 135.  
     Dichromate, 135.  
     Ferri cyanide, 135.  
     Ferrocyanide, 135.

Potassium Hydrogen Sulphate, 135.  
 Hydrogen Tartrate, 53, 56, 64.  
 Hydroxide, 69, 135.  
 Iodide, 135.  
 Nitrate, 52, 56, 57, 135.  
 Permanganate, 123, 135.  
 Oxidation by, 246.  
 Sulphate, 135.  
 Powder (Black Gunpowder), 3.  
 'Precipitate, White,' 102.  
 Precipitation, Conditions of, 90.  
 Prussian Blue, 192.

Q.

Qualitative Analysis, 75.  
 Anions, 75.  
 Kations, 76.  
 Quicklime, 129.

R.

Radicles, 75.  
 Realgar, 109.  
 Reducing Flame, 82.  
 Respiration, 28.  
 Reversible Reactions, 31.

S.

Sal Ammoniac, 133.  
 Salt, Definition, 21, 50.  
 Acid, }  
 Basic, } 50.  
 Double, }  
 Normal, }  
 Glauber's, 56, 65.  
 Salts, Methods of Preparation, 51.  
 Saturated Solution, Definition, 11.  
 Selenite, 129.  
 Shot, 99.  
 Silicon, 43.  
 Silver, 95.  
 Arsenate, 95.  
 Bromide, 95.  
 Chloride, 94, 95.  
 Chromate, 95, 119.  
 Compounds, Tests for, 94.  
 German, 101.  
 Iodide, 94, 95.  
 Nitrate, 94, 95.  
 Oxide, 94, 95.  
 Phosphate, 95.  
 Slaked Lime, 57, 70.  
 Soda, Caustic, 138.  
 Crystals, 138.  
 Washing, 138.  
 Sodium, 137.  
 Aluminate, 115.

Sodium Amalgam, 103.  
 Arsenite, 109.  
 Bicarbonate, 56, 65, 137.  
 Carbonate, 56, 66, 138.  
 Chloride, 137.  
 Compounds, Tests for, 136.  
 „ List of, 137.  
 Hydrogen Carbonate, 56, 65, 137.  
 Hydroxide, 69, 138.  
 Metasilicate, 138.  
 Nitrate, 137.  
 Nitrite, 137.  
 Oxide, 138.  
 Peroxide, 118, 138.  
 Phosphate, Common, 56, 65, 138.  
 Pyroborate, 65.  
 Sulphate, 65, 137.  
 Sulphide, 138.  
 Sulphite, 137.  
 Tetraborate, 65.  
 Thiosulphate, 137.  
 Zincate, 120.  
 Solder, 99.  
 Solubilities, 186, 187, 188, 189.  
 Solution, Definition, 10.  
 Stannic Chloride, 113.  
 Compounds, Tests for, 112.  
 „ List of, 113.  
 Oxide, 34, 112, 113.  
 Sulphide, 112, 113.  
 Stannous Chloride, 112, 113.  
 Compounds, Tests for, 112.  
 „ List of, 113.  
 Nitrate, 113.  
 Oxide, 113.  
 Sulphate, 113.  
 Sulphide, 112, 113.  
 Stibnite, 111.  
 Strontium, 127.  
 Carbonate, 126, 127.  
 Chloride, 127.  
 Compounds, Tests for, 126.  
 „ List of, 127.  
 Nitrate, 127.  
 Oxide, 127.  
 Sulphate, 126, 127.  
 Sublimate, Corrosive, 103.  
 Sublimation, 14.  
 Sulphantimoniates (see Thioanti-  
 moniates).  
 Sulpharsenates (see Thioarsenates).  
 Sulphate Ion (Sulphion).  
 Sulphates, 185, 186, 196, 207.  
 Sulphides, 40, 186, 191, 206.  
 Sulphites, 185, 186, 194, 207, 209.  
 Sulphur Dioxide, 41.  
 Trioxide, 42.  
 Sulphuretted Hydrogen, 39, 191.  
 Sulphuric Anhydride, 42.  
 Sulphurous Anhydride, 41.

## T.

Tap Water, Impurities, 25.  
Tartar Emetic, 56, 64.  
Tartrates, 185, 188, 205, 209.  
Temperature, Influence on Precipitation, 90.  
Thioantimoniates, 110.  
Thioarsenates, 106.  
Tin, 113.  
    (See Stannous and Stannic Compounds.)  
Tinstone, 113.  
Turnbull's Blue, 116.  
Type Metal, 99.

## U.

Units of Measurement, 250.

## V.

Valency, Common, 5.  
Vermilion, 103.  
Vitriol, Blue, 61.  
    Green, 62.  
    White, 62.  
Volumetric Analysis, 230.

## W.

Wash Bottle, 9.  
Washing Soda, 56, 66, 138.  
Water, 25.  
Water-bath, 25.  
Water Vapour in Air, 28.  
Weighing Bottle, 227.  
Weights, Atomic, 251.  
White Lead, 99.  
Witherite, 125.

## Z.

Zinc, 121.  
    Blende, 121.  
    Carbonate, 121.  
    Chloride, 121.  
    Compounds, Tests for, 120.  
        " List of, 121.  
    Hydroxide, 57, 70, 120, 121.  
    Oxide, 121, 210.  
    Sulphate, 62, 121.  
    Sulphide, 120, 121.  
    White, 121.



OXFORD: HORACE HART  
PRINTER TO THE UNIVERSITY





[illegible]

APR 29 1932

2842

D2842  
practical

R 20 1932

SCHOOL LIBRARY

